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A Feasibility Study of Ozone Remote-Sensing by Laser-Induced Infrared Fluorescence.

John Louis Guagliardo
Louisiana State University and Agricultural & Mechanical College

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A FEASIBILITY STUDY OF OZONE REMOTE SENSING BY LASER INDUCED INFRARED FLUORESCENCE

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University
and Agricultural and Mechanical College
in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

in

The Department of Chemistry

by

John Louis Guagliardo
B.S., Southeastern Louisiana University, 1967

May, 1973

Dedication

This work is dedicated to the people who at one time or another made the end possible by providing the means; the Allens, the Davids, the Guagliardos, and Mrs. Elsie Waldrop; but most of all, to Elaine.

Acknowledgement

The author wishes to acknowledge the help and guidance of his research director, Dr. James W. Robinson, who gave the author the proverbial second chance. The author hopes that Dr. Robinson's faith in him was justified.

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ABSTRACT

The objective of this work was to study the fluorescence of ozone induced by its exposure to a carbon dioxide laser. The work was divided into three parts: (1) The construction and testing of a continuous, tunable carbon dioxide laser; (2) A study of the analytical parameters involved in developing a procedure for the remote sensing of ozone based on laser induced infrared fluorescence; and (3) A short attempt at actual remote sensing.

A carbon dioxide laser was built which was tunable over the range of 9.2 to 10.8 microns. This laser was found to be much more stable than commercial non-tunable lasers, but not quite as powerful.

Fluorescence was observed for concentration of about one per cent ozone from a 0.6 milliliter volume. Absolute analytical sensitivity then was found to be seventy micrograms of ozone. To carry out this study an ozone generator was made and a procedure developed to determine the concentration of ozone generated.

It was found that the fluorescence intensity was proportional to the laser intensity. This indicated that fluorescence intensity would be enhanced by using more powerful lasers. It was also found that the fluorescence intensity

was very sensitive to minor changes in wavelength of the laser beam. This permits selective analysis by measuring the fluorescence intensity when the laser beam (a) excited ozone, and (b) did not excite ozone.

It was also found that absorption of radiation by the laser was dependent on the same small changes of laser wavelength.

Based on the data obtained, it seemed evident that by using more intense lasers, and more sensitive detectors (which are now available commercially), a remote sensing device for ozone detection could be built.

HISTORICAL PREFACE

Ozone has been noticed by its smell during thunderstorms since ancient times. Homer's Iliad and Odyssey mention this.

Ozone was first produced "artificially" in 1786 by the passing of sparks through oxygen. A decrease in volume was noted. The establishment of the correct triatomic formula was not accepted until the late nineteenth century. This was mainly due to the fact that ozone was only available in a very dilute form in oxygen. This situation delayed the precise determination of its molecular weight.

Analysis of clean, dry air at sea level gives a concentration of ozone of about 0.02 parts per million.[1] The ozone concentration rises appreciably with altitude, both relatively and absolutely, and reaches a maximum at approximately twenty-five kilometers. This concentrated ozone layer is an efficient absorber of solar short-wave ultraviolet radiation (less than 3000 angstroms); thus protecting life on earth from the harmful effects of the radiation.

Atmospheric ozone is formed mainly by high-altitude, photochemical synthesis from molecular oxygen which occurs by absorption of solar radiation of less than 2000 angstroms.[2]

The concentrated ozone layer at twenty-five kilometers is a warm layer due to the heat generated by light absorption and by exothermic decomposition of ozone. This layer plays an important part in the temperature regulation of the lower atmosphere.[3]

The oxidant levels (oxidant being chiefly ozone) in large cities in the United States deviate substantially from the background level. This fact can be seen from Table 1.

The level of oxidants, hydrocarbons, and oxides of nitrogen can be seen to be related, as shown in Figure 1, and from the following reaction scheme:

NO_2 + light = NO + O

O + O_2 = O_3

O_3 + NO = NO_2 + O_2

O + Hc (hydrocarbon) = $HcO\cdot$

$HcO\cdot$ + O_2 = $HcO_3\cdot$

HcO_3 + Hc = Aldehydes, Ketones, etc.

HcO_3 + NO = HcO_2 + NO_2

HcO_3 + O_2 = O_3 + $HcO_2\cdot$

HcO_x + NO_2 = Peroxyacyl Nitrates[4]

It has been stated that ozone might be one precursor to singlet oxygen.[5] Singlet oxygen has been used to explain a number of unusual biological effects observed in humans, animals, and plants.[6]

Table 1

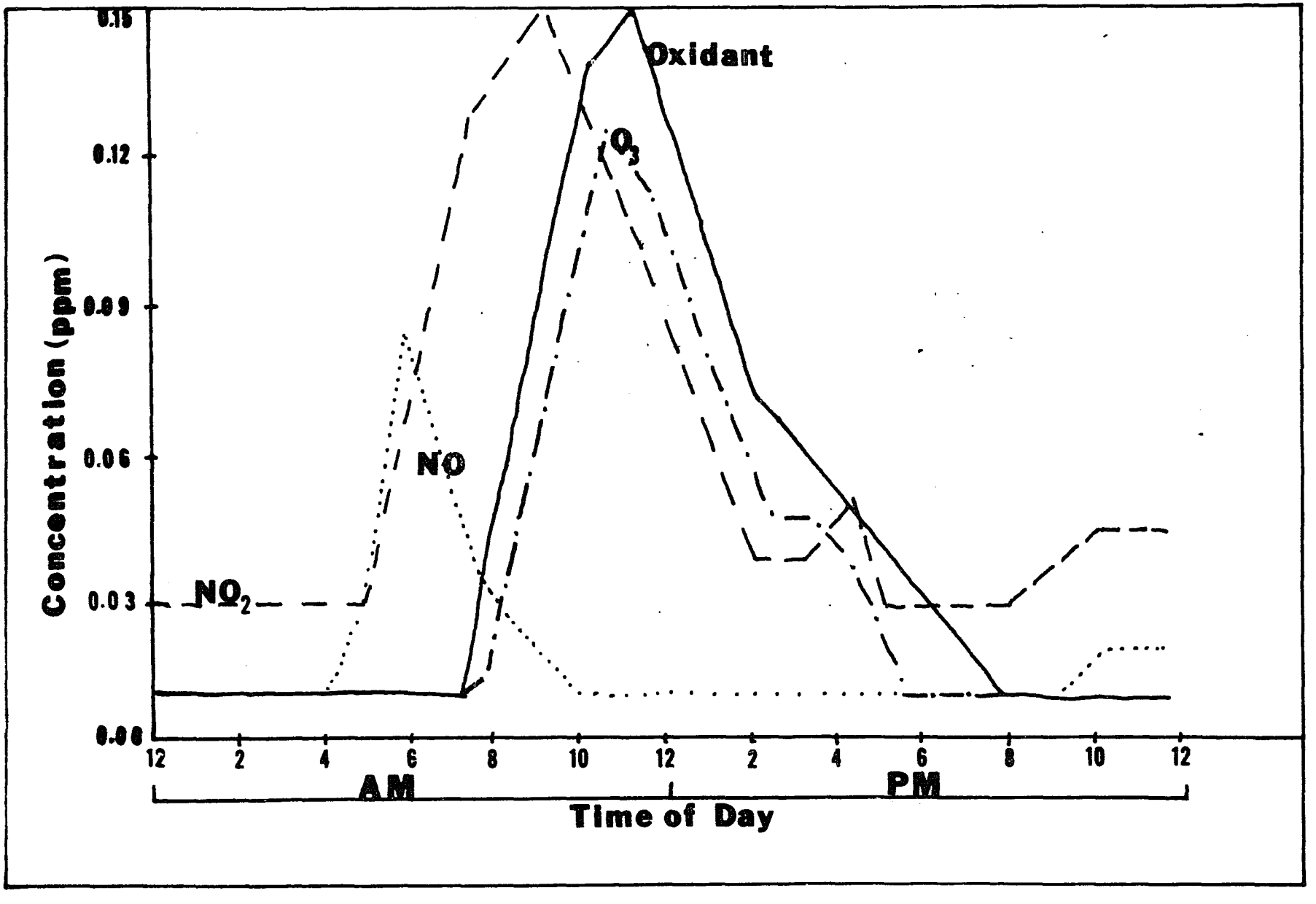
SUMMARY OF MAXIMUM HOURLY OXIDANT LEVELS FOR EIGHT U.S. CITIES, 1964-1965, FROM CONTINUOUS AIR MONITORING STATIONS[7]

City	Year	Days Of Valid Data	Days having maximum hourly oxidant equal to or greater than indicated concentration: 0.15 ppm No.	0.15 ppm %	0.10 ppm No.	0.10 ppm %	0.05 ppm No.	0.05 ppm %
Chicago	1964	254	0	0	15	6	149	59
	1965	275	0	0	9	3	120	44
Cincinnati	1964	303	5	1.5	36	12	137	45
	1965	310	5	1.5	19	6	182	59
Denver	1965	285	14	5	51	18	226	79
Los Angeles	1964	349	83	24	149	42	221	63
	1965	365	121	33	185	51	275	75
Philadelphia	1964	289	9	3	37	13	124	43
	1965	266	4	1.5	23	9	109	41
St. Louis	1964	253	6	2.5	26	10	156	62
	1965	329	8	2.5	33	10	206	63
San Francisco	1964	298	1	.5	13	4	72	24
Washington	1964	293	4	1	40	14	163	56
	1965	284	3	1	25	9	150	53

Figure 1

DIURNAL VARIATION OF POLLUTANTS IN LOS ANGELES

JUNE 19, 1965[8]


0.15
0.12
0.09
0.06
0.03
0.00
Concentration (ppm)
Oxidant
O_3
NO
NO_2
12
2
4
6
8
10
12
2
4
6
8
10
12
AM
PM
Time of Day

The haze that is seen over polluted cities is one of the most obvious manifestations of photochemical smog. Visibility is reduced because the light is scattered off of particulates, and (particularly in the case of smog) aerosol droplets. These species are usually between 0.1 and 1 micron in diameter.

> ". . . results indicate that two distinct types of aerosol (sulfate and carbonaceous) can be formed by some of the gaseous contaminants of urban atmospheres. Ozone appears to be a key reactant in the formation of both types, and irradiation and nitric oxide may be involved only to the degree that they form ozone."[9]

The effects of ozone on man have been investigated for a long time. It was found that ozone had a sedative effect long before the low-concentration, injurious effects were discovered.[10]

In one experiment, one of the investigators voluntarily exposed himself to 1.5 parts per million of ozone for one-half hour, and then to a lesser concentration for one and one-half hours.[11] The immediate responses were dryness of the mouth and throat, and a reduced ability to concentrate and think. The subject felt chest pains and had altered taste sensation. After two days a cough developed. The chest pains subsided after the second day, but the cough persisted for two weeks.

The following is a summary of experiments on the toxicity of ozone on some animals:

> "Repeated exposures of 2.4 parts per million by volume of ozone induced some hemorrhage and edema in lungs of rats. Adaptation to ozone was noted after thirty-two hours of accumulated exposure. Twenty per cent of 102 mice died after continuous exposure to 2.4 parts per million by volume of ozone for twenty-four hours. Chronic exposure to ozone decreased the weight gain of young rats and concentrations greater than 1.2 parts per million by volume and longer than seven hours per day significantly affected their growth. The 0.1 part per million value as the maximum allowable concentration of ozone for an eight hour day appears reasonable."[12]

These and other data have led to the establishment of air quality standards. There are three levels defined in the California Air Quality Standards.[13]

The first is the "Adverse Level" at which there will be sensory irritation, damage to vegetation, reduction in visibility or similar effects. (For ozone, this is 0.15 part per million for one hour.)

The second is the "Serious Level" where there is alteration of bodily function, or a likelihood of leading to chronic disease. This is what is said of ozone: Ozone, at one part per million for eight hours daily for about one year has produced bronchiolitis and fibrositis in rodents.[14]

Extrapolation of these data to man is difficult. Functional impairment data have been reported; at 1.25 parts per million some effects were observed on residual volume and

diffusing capacity. The variability of these tests was not reported. Additional data would be needed before a standard is set.

The third is the "Emergency Level" at which it is likely that acute sickness or death in sensitive groups of persons will occur. A concentration of ozone of 2.0 parts per million for one hour may produce serious interference with function in healthy persons, and the assumption is made that this might cause acute illness in sensitive persons.

It has been reported that there are characteristic differences in the damage caused to leaves by ozone and that caused by photochemical oxidants.[15] Ozone causes the appearance of characteristic dark spots on the upper surfaces of leaves. Such damage has been observed in pinto beans[16] and tobacco[17] after exposure to only 0.2 and 0.1 milligrams per cubic meter for four hours, respectively. It was found that oxidants inhibit photosynthesis, suppress growth, and increase the abscission of leaves.[18]

Ozone also damages materials; it cracks rubber, weakens fabrics, and fades dyes.[19]

Over the past several years, studies of laser-induced infrared fluorescence have been reported.[20-24] These studies were carried out on about fifty compounds. Many of the compounds absorbed the laser radiation and fluoresced strongly.

Some of these compounds such as methane, nitromethane, chloroform, carbon disulfide, nitrous oxide, and sulfur dioxide did not appreciably absorb at the laser wavelength (10.6 microns). Nevertheless, it was found that they did fluoresce, though at a relatively low intensity.

Recently, there has been some disagreement on the mechanism of the excitation and subsequent fluorescence[25] by the molecule. It has been stated that resonance absorption is necessary for emission to occur; however, results indicate that fluorescence occurred at wavelengths other than that at which absorption took place.

Also, the fact that the emission observed was not thermal in origin has been demonstrated[20-24] and has been confirmed by other workers for the case of methane.[26] Although thermal excitation is always possible within the laser beam, fluorescence (i.e., radiation-induced excitation) is also encountered.

It has also been shown that, for a given pressure, the emission and absorption bands coincide in wavelength, indicating that the same vibrational energy levels are involved.[20-24] The high-resolution studies with ethylene seem to show additionally that the same vibrational and rotational levels are involved.[27] The absorbed energy, even at fairly low pressures, is distributed amongst the rotational

states over a period of microseconds, whereas vibrational relaxation and emission take place in milliseconds.[28]

Insight into the relaxation times was gained when infrared double-resonance studies were performed on sulfur hexachloride.[29] It was found that absorption of a strong pulse of laser light produced a "hole" in the absorption spectrum.

The population of the upper rotational states was increased and this led to reduced absorption because there were fewer molecules in the rotational ground state. The hole formed in the absorption spectrum was rapidly filled by the rotational relaxation processes. The vibrational energy redistributed itself through very efficient vibration-vibration energy transfer.

Part I

INTRODUCTION

INTRODUCTION

There are presently a number of methods for the determination of ozone; many of these are cited in a paper by Sachdev, Lodge, and West.[30] In that publication, the authors presented an excellent method which is a modification of the West-Gaeke procedure. This technique utilizes scrubbing the ozone from a known volume of air and analyzing the scrubbing solution for the reaction products from ozone.

Scrubbing techniques suffer from several problems, one of which is that the ozone may decompose in the scrubbing process and cause low analytical results to be obtained. Even when the problems of sample decomposition have been overcome, there remains the difficulty that all samples must be taken in situ.

This means that the sampler can only monitor one geographic point at a time. Also, many locations cannot be sampled because of the physical difficulties involved in reaching them. Further, the localized sampling potential negates the possibility of clandestine sampling of suspected sources of pollution. Finally, in order to evaluate a large geographic area, a large number of samples must be taken. This is a time-consuming, expensive operation. Also, the data are not in real time (i.e., the results are obtained

some period after the sample was taken.) This prevents continuous monitoring of air levels and makes effective control virtually impossible.

Remote sensing requires no sample collection. Ideally, the equipment would be sufficiently portable to be moved from station to station. When set up in a location, remote sensing equipment could be used to monitor an area, depending on the range of the equipment.

It is pertinent to note that ozone has a strong absorption band within the range of a tunable carbon dioxide laser. It was felt that if a tunable carbon dioxide laser were built, it would be possible to do feasibility studies on the use of infrared fluorescence as a remote sensing method for ozone, as well as other compounds.

The problem can be divided into three parts: (1) the construction of the tunable laser and detection system, (2) the gathering of data within the laboratory on ozone; and (3) a short attempt at actual remote sensing.

Except for the fact that the output power was not as high as had been hoped, the laser was successfully constructed. It has proved to be satisfactory for all the experiments which were conducted in the laboratory with samples contained in gas cells.

The laser-induced infrared fluorescence studies on ozone, albeit necessarily done at high concentration, were successful.

Feasibility studies on a number of ozone phenomena were done. The relationship between excitation wavelength and fluorescence intensity and wavelength was studied. The sensitivity of the system was calculated. Due to the small volume which was "seen" by the detection system, it was calculated that even though the concentration was high, the number of molecules giving rise to the signal was small. Attempts at improving the optical system so that the concentration of ozone could be decreased were not successful.

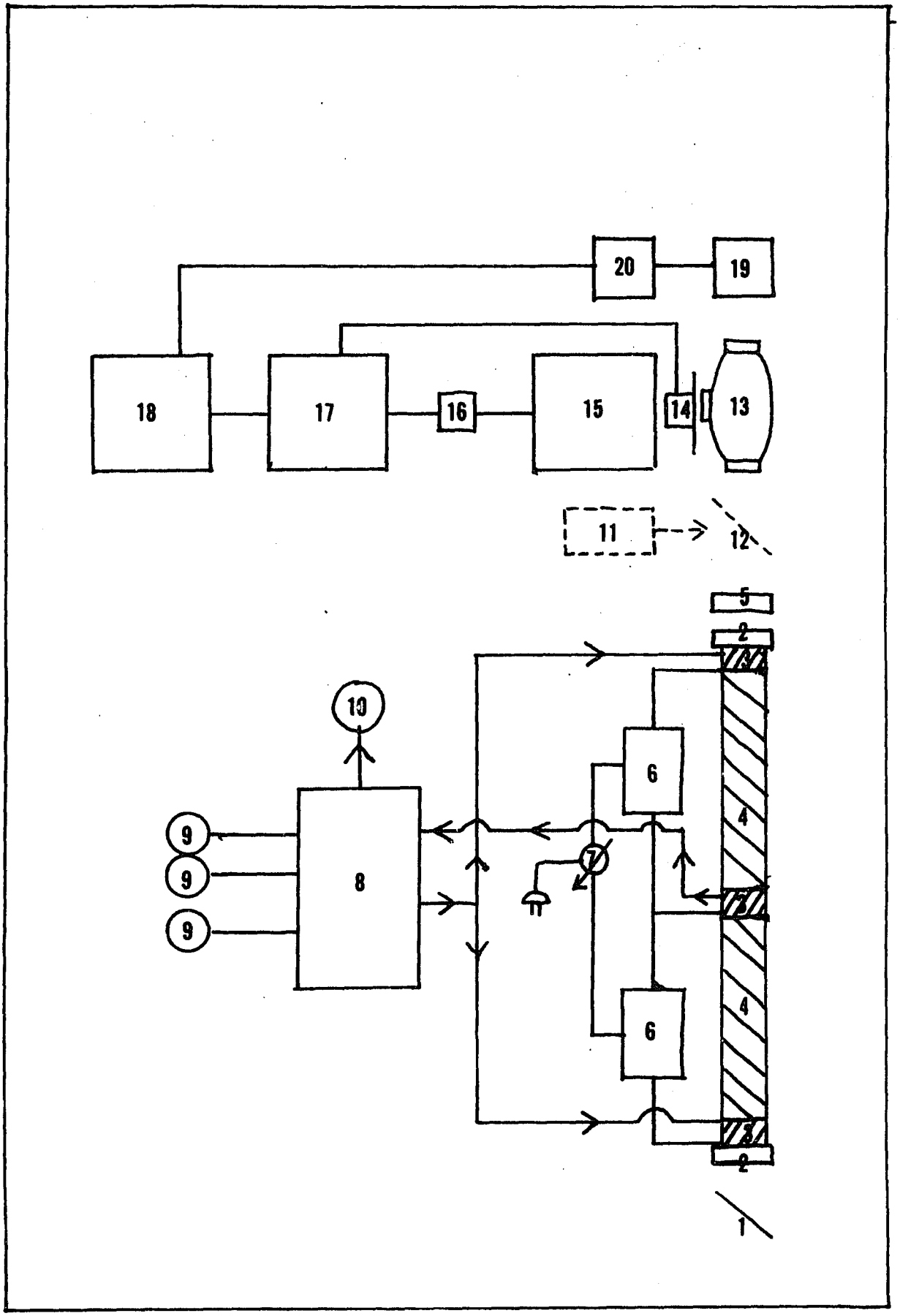
A diagram of the fluorescence system showing the various components which will be discussed in the next section is shown in Figure 2. There were three lasers used in this study. The construction of a tunable carbon dioxide laser is discussed. A commercial molecular (carbon dioxide) laser manufactured by Perkin-Elmer is mentioned at various places; and a helium-neon laser which was used exclusively to facilitate alignment is also mentioned.

After the construction of the tunable laser and the gathering of data on ozone was completed, it was felt that a crude attempt at actual remote sensing would be tried. This would give an insight into the problems with the equipment which would be encountered when a more sophisticated attempt was made. Although no hard data were obtained, problems which were unsuspected hithertofore (e.g., divergence) were recognized and steps at correcting them can be made in the future.

Figure 2

LASER INDUCED INFRARED FLUORESCENCE APPARATUS

1. Grating (Rear Laser Mirror)
2. Window Holder
3. Electrode
4. Water-Jacketed Glass Plasma Tube Parts
5. Output Mirror
6. Neon Sign Transformers
7. Variac
8. Flow Control
9. Gas Cylinders
10. Vacuum Pump
11. Helium-Neon Laser (used during alignment)
12. Beam Splitter (used during alignment)
13. Fluorescence Cell
14. Chopper
15. Monochromator-Detector
16. Preamplifier
17. Amplifier
18. Dual-Pen Recorder
19. Power Meter Head
20. Power Meter Amplifier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Lasers are available today with peak powers on the order of a megawatt. The laser used in this study had an average output power of only eight watts. If pulse type lasers can be applied to laser-induced infrared fluorescence, then this would increase the sensitivity greatly. In addition, by going to a cryogenic detection system, the sensitivity could be further increased by about two orders of magnitude. If these factors are additive (and there are indications that they are), an increase in sensitivity of about a factor of 10^7 could be realized. Laser power and detector sensitivity will probably increase in the future, therefore this method merits continued investigation.

Part II

DESCRIPTION OF EQUIPMENT

CONSTRUCTION OF THE LASER

The discussion of the equipment used in the construction of the laser will be divided into three parts: (1) the power supply; (2) the flow control; and, (3) the laser cavity.

Power Supply

A very simple power supply was used. Two 15,000 volt, 30 milliamp current-limited transformers were used. These were neon sign transformers which were purchased from a neon sign concern in this city. In addition, two 15,000 volt, 120 milliamp transformers were ordered directly from the manufacturer, General Electric.

The input voltage was varied by using a 115 volt, 20 amp Variac. This, along with the transformers, constituted the power supply.

At times, various current and voltage measuring devices were inserted in the circuit, but these were only temporary.

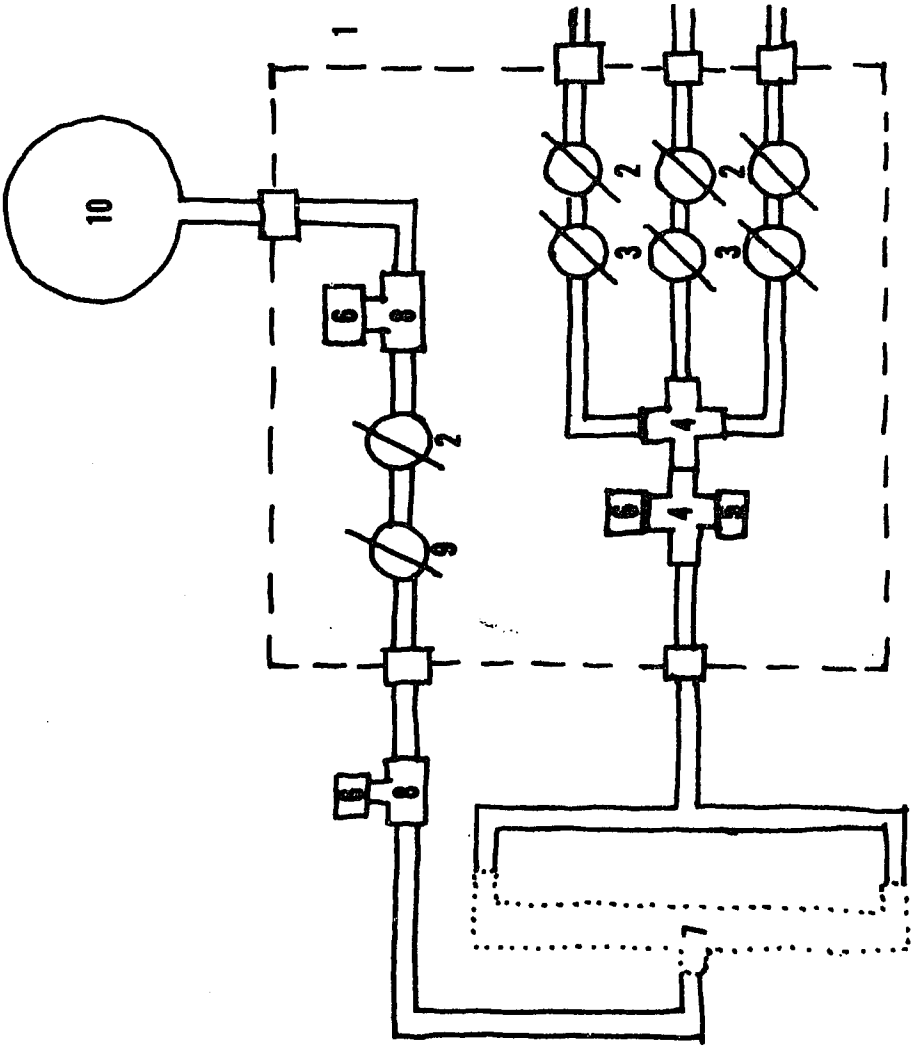
Flow Control System

The gas used in this tunable laser was a mixture of carbon dioxide, nitrogen, and helium. A diagram of the entire flow system with the flow control module is shown in Figure 3.

Figure 3

FLOW CONTROL SYSTEM

1. Flow Module Housing
2. Shutoff Valves
3. "Fine" Metering Valves
4. Swagelok Union "T"s
5. Swagelok Plug
6. Thermocouple Gauge
7. Plasma Tube (dotted)
8. Swagelok "T"
9. "Very Fine" Metering Valve
10. Vacuum Pump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All the tubing used between the gas cylinders and the plasma tube was one-quarter inch polyethylene. Tubing from the plasma tube to the vacuum flow regulator valve, and then from the regulator valve to the vacuum pump was one-half inch polyethylene.

The shutoff valves were of the Nupro "H" series bellows type (brass). Flow regulation between the gas cylinders and the plasma tube was accomplished using Nupro very fine micrometer metering valves. Flow regulation between the vacuum pump and the plasma tube was accomplished using a Nupro "BM" series bellows metering valve. A Nupro safety relief valve was used to "bleed" air into the system when the vacuum pump was turned off.

All the fittings used in the flow system were of the Swagelok brass type.

The pressure at various points was monitored using a Veeco TG-27 thermocouple gauge control. With this, Veeco type DF-4AM vacuum gauge tubes were used.

A Welch Duo-Seal Model 1397 vacuum pump was used in this system because of its high flow rate.

Laser Cavity

The laser was designed to have three electrodes and a water-cooled jacket. It was felt that if the electrodes were sealed through the water jacket, the thermal differences

between the water-cooled glass and the electrode-heated glass would prove to be too great a stress. Therefore, it was necessary to separate the electrodes from the water jacket in some way. To accomplish this, the water-cooled glass part was divided into two sections. Each section had standard-taper 29/42 female fittings at each end. Then, aluminum pieces were made that would serve as both electrodes and acceptors for the Swagelok fittings of the flow system. Figure 4 shows the pieces which made up the plasma tube. Teflon sleeves were used on all the standard-taper pieces.

The laser was made tunable by using an 1800 groove per inch gold-coated original aluminum grating blazed for twenty-two degrees, (10.6 microns). The windows were antireflection-coated on one side, and twenty per cent reflecting on the other side. The grating, windows, and mirror were supplied by Oriel Optics Corporation.

The laser cavity was mounted on an Oriel 2.44 meter optical bench. The grating and output mirror were mounted on precision mirror mounts, also supplied by Oriel. The mount for the grating had a translation stage on it with micrometer adjustment so that small changes in cavity length could be made.

The plasma tube was supported by four mounts which were constructed in the University Machine Shop. Each was a ring which could be mounted on the optical bench. There were

Figure 4

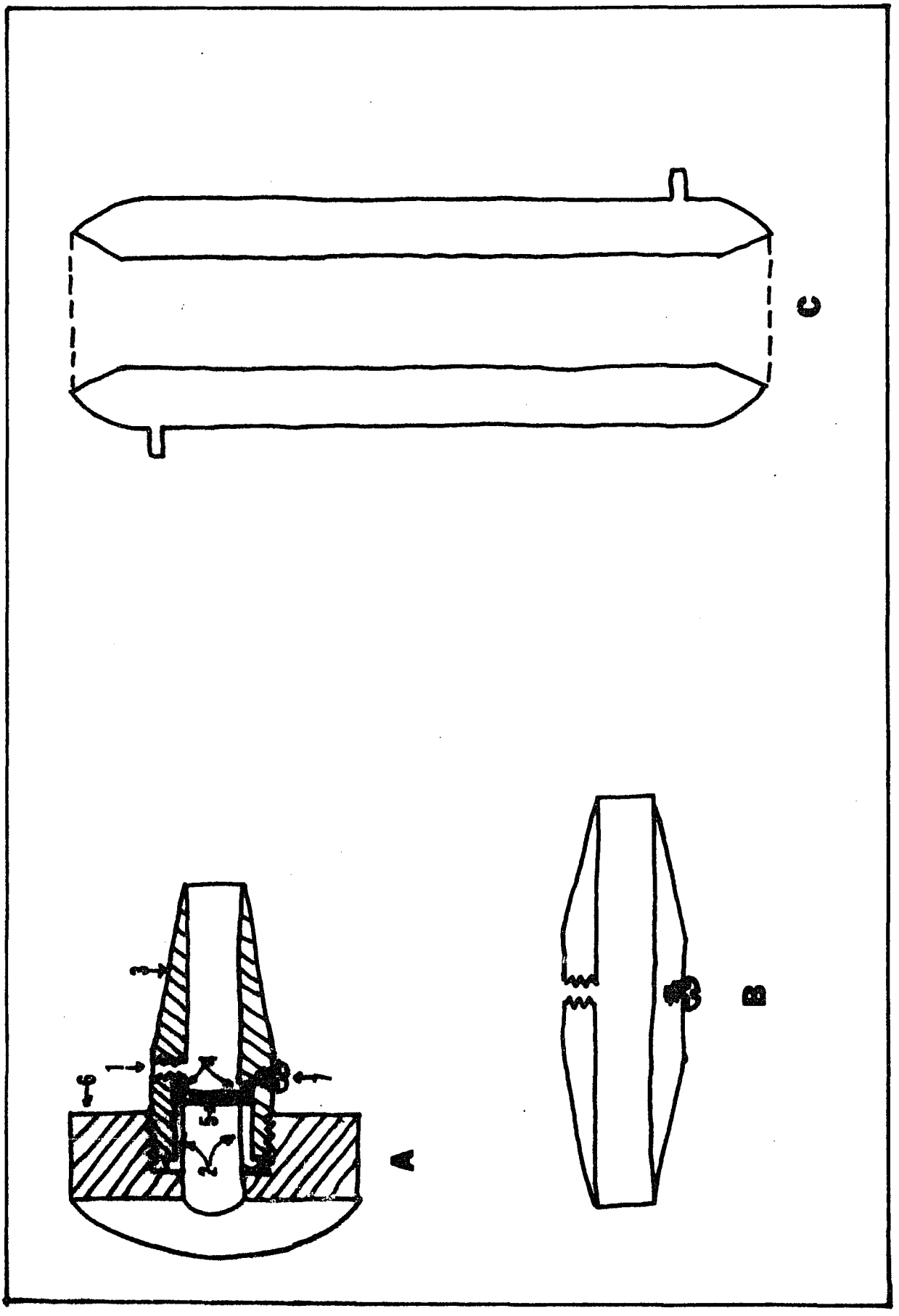
PLASMA TUBE PIECES

A. End Electrode

1. ¼" Pipe Thread Hole
2. Mirror Retainer
3. Aluminum Standard Taper
4. "O" Ring
5. Germanium Window
6. Polyvinyl Chloride
7. Screw for Connection to Power Supply

B. Middle Electrode

C. Glass Tube Half


C
B
A

three screws through each ring, 120 degrees apart. These screws supported the tube and provided it with some adjustment. Each ring could be taken in half so that the cavity could be disassembled easily.

DETECTION SYSTEM

Monochromator

A McPherson 0.3 meter Model 218 monochromator was used with a 150 groove per millimeter grating blazed for six microns.

Detector

Onto the monochromator was mounted a Barnes Model 662 Triglycene Sulfate (T.G.S.) pyroelectric detector with a Metal Oxide Semiconductor Field Effect Transistor (MOSFET) pre-amplifier.

Amplifier

The amplifier used was a Princeton Applied Research (P.A.R.) Model 124 lock-in with a P.A.R. Model 116 differential preamplifier.

Chopper

The Model 124 was locked in on a P.A.R. Model 125 chopper which was usually operated at 26.2 Hz.

Power Monitor

To make various power measurements, but mainly to monitor the laser radiation transmitted through the sample cell, a Coherent Radiation Model 201 power meter was used.

Recorder

Both the output signal from the P.A.R. amplifier and the output signal from the power monitor were fed into a Texas Instruments Servo-Riter II ten-inch dual pen recorder.

Helium-Neon Laser

A Meterologic 0.5 watt helium-neon laser was used for purposes of alignment.

OZONE GENERATOR

Two types of ozone generators were tried. The first was a large glass vessel containing a General Electric OZ-4 bulb. The oxygen was passed through the vessel and the effluent contained ozone in the part per million concentration range.

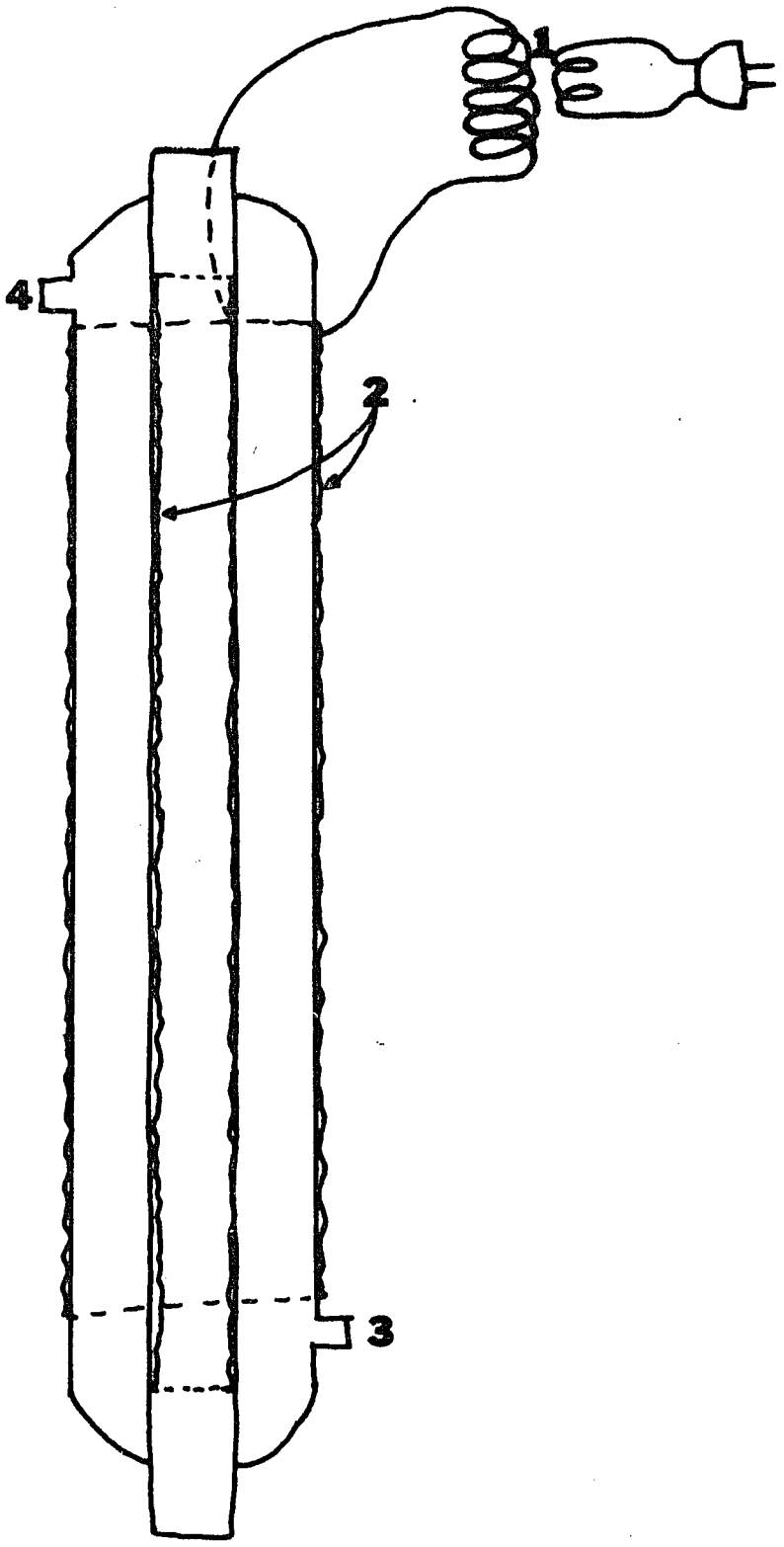
The other type of generator used was a modified "silent-discharge" apparatus. This utilized a small West condensor. Aluminum foil was wrapped around a piece of glass tubing and inserted inside the West condensor. The outside of the condensor was then wrapped with foil, also. The leads from a 15,000 volt, 120 milliamp current-limited transformer were hooked up, one each, to the inner and outer layers of foil. When the transformer was connected to line current, there was a "silent discharge" from the two layers of foil through the intervening two layers of glass and air space in the dry water jacket. When oxygen was passed through the water jacket, it was excited by the electronic discharge and formed ozone in the per cent concentration range.

This apparatus is shown in Figure 5.

Figure 5

OZONE GENERATOR

1. Transformer
2. Aluminum Foil
3. Oxygen Inlet
4. Ozone-Oxygen Outlet


1
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3

CELLS

Three cells were tried in this study. The first was a simple all-glass cell with the windows affixed with epoxy cement. There were three windows, each of IRTRAN II (Polycrystaline Zinc Sulfide) supplied by Eastman Kodak.

The second cell had the two windows through which the laser beam passed mounted on 24/40 standard-taper male joints so that they could be removed. The third window, the fluorescence window, was secured in a metal "O" ring mount which had been cemented to the glass of the cell.

These two cells are shown in Figure 6.

The third cell employed a Dall-Cassegrainian mirror system for concentration of the fluorescence. This cell is shown in Figure 7.

The mirror system was mounted in an aluminum cylinder sealed by an aluminum plate. Through this plate passed the shafts which supported the 4¼-inch aluminum-coated primary mirror. Both the shafts and the plate were sealed with "O" rings. Also in this plate were two more one-inch "O" ring-sealed holes in which were placed IRTRAN II windows. In most cases, the "O" rings were protected from the ozone by a thin coat of parafin wax.

Figure 6

SMALL CELLS

A. 20 Centimeter Cell

1. IRTRAN II Windows
2. Sample Inlet and Outlet
3. Female Standard Taper
4. Male Standard Taper
5. "O" Ring Window Holder

B. 44.5 Centimeter Cell

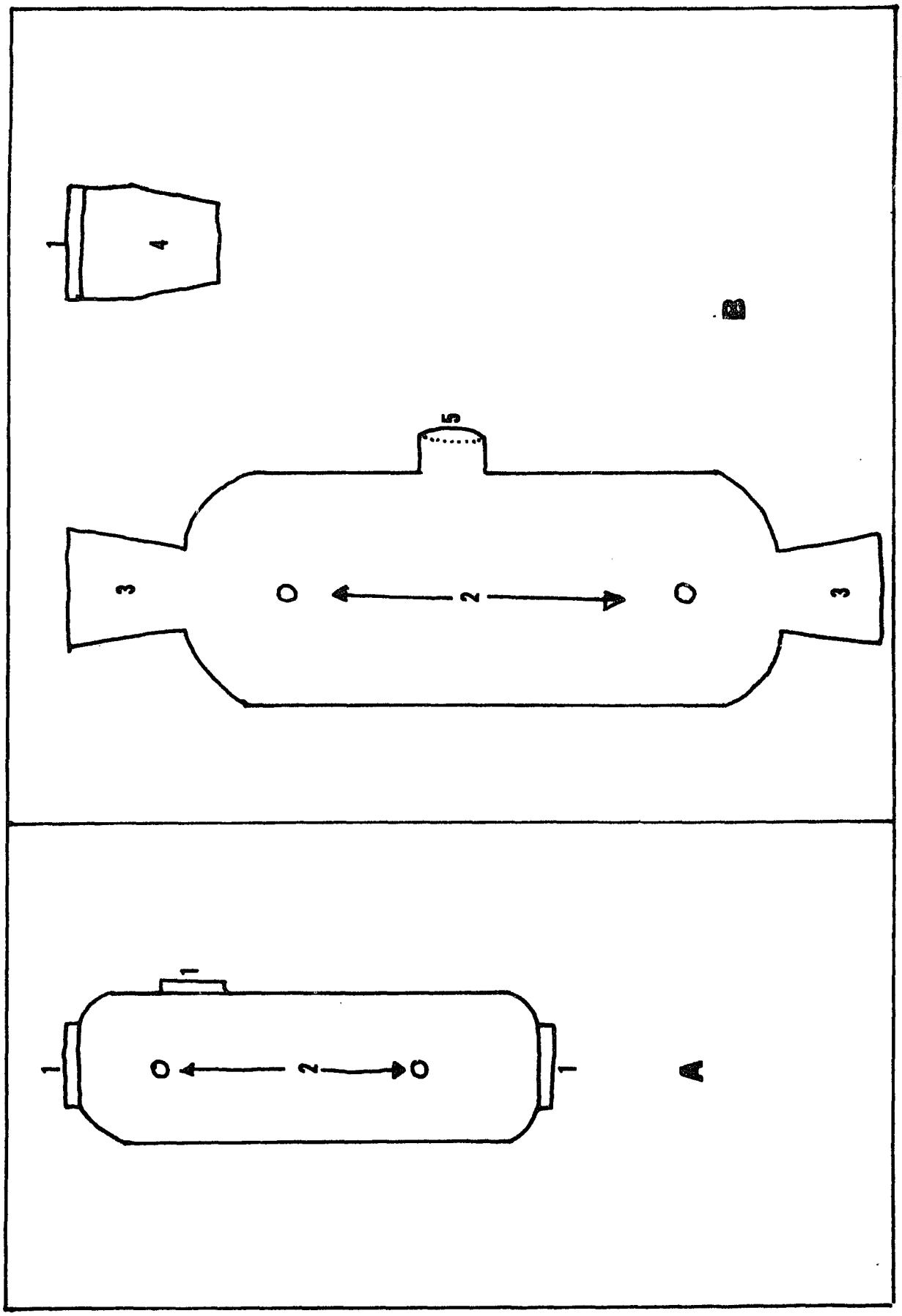
1
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Figure 7

LARGE CELL

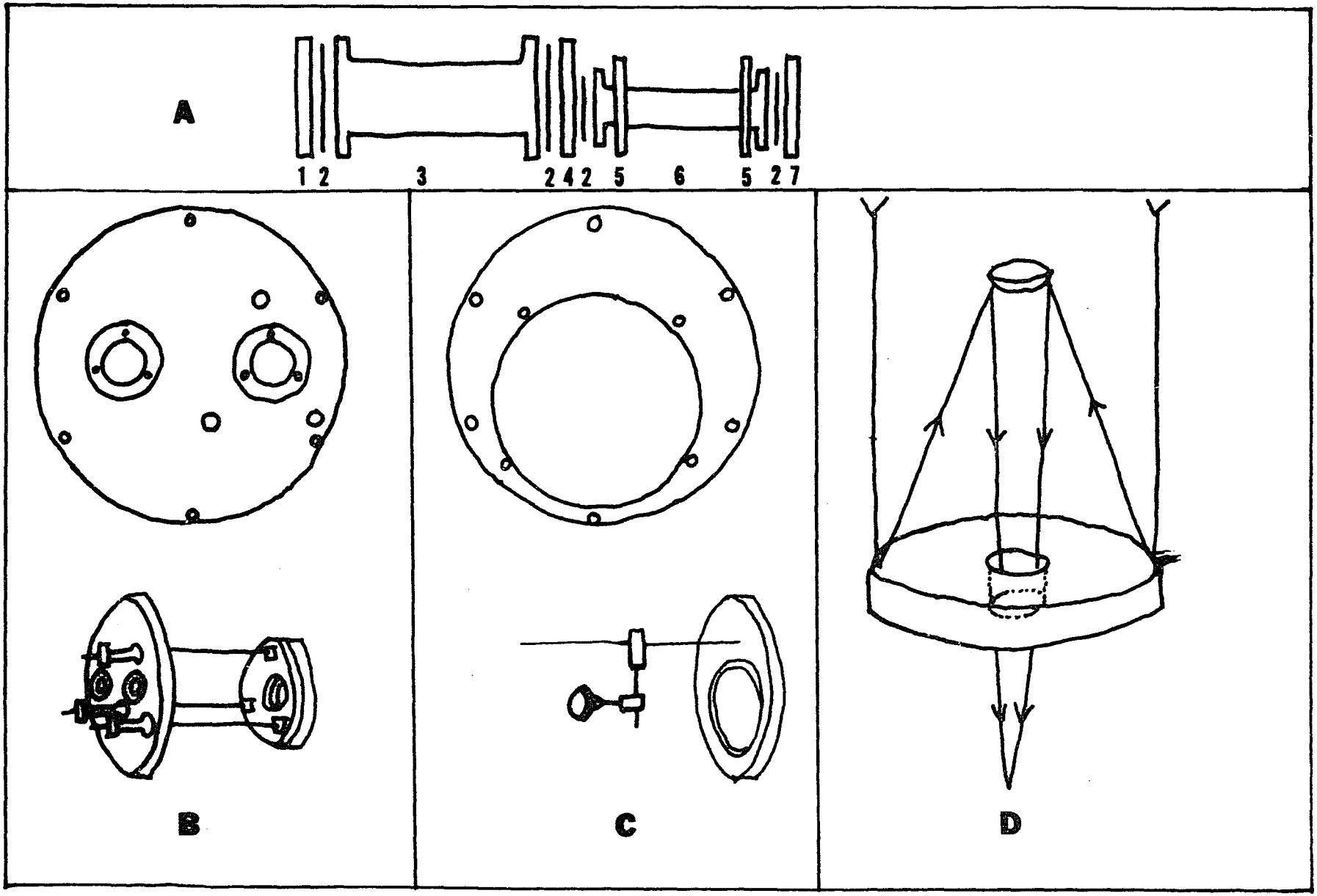
A. Exploded View

1. Front Plate
2. "O" Ring
3. Steel Tube
4. Reduction Plate
5. Securing Rings
6. Glass Tube
7. Back Plate

B. Front Plate with 4¼-inch Primary Mirror

C. Reduction Plate with 1¼-inch Secondary Mirror

D. Cassegrainian Optical System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5 2 7
B
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D

The secondary mirror was mounted on a shaft running lengthwise in the cell so that the focal length of the mirror system could be changed. All shafts and mirror mount parts were made of brass.

To the aluminum cylinder was attached a cylinder of glass. It was felt that if any reactions occurred which led to liquid or solid formation, they could be seen immediately if part of the cell was glass. To the back of the glass cylinder, an aluminum plate was sealed. In this aluminum plate there was an "O" ring seal hole for accepting an IRTRAN II window. The plate was sealed to the glass cylinder, and the glass cylinder to the aluminum cylinder with "O" rings.

There were Swagelok one-quarter inch fittings in both plates--two in the back plate and one in the front. It was through these fittings that the sample entered the cell.

Part III

RESULTS AND DISCUSSION

LASER OPERATING PARAMETERS

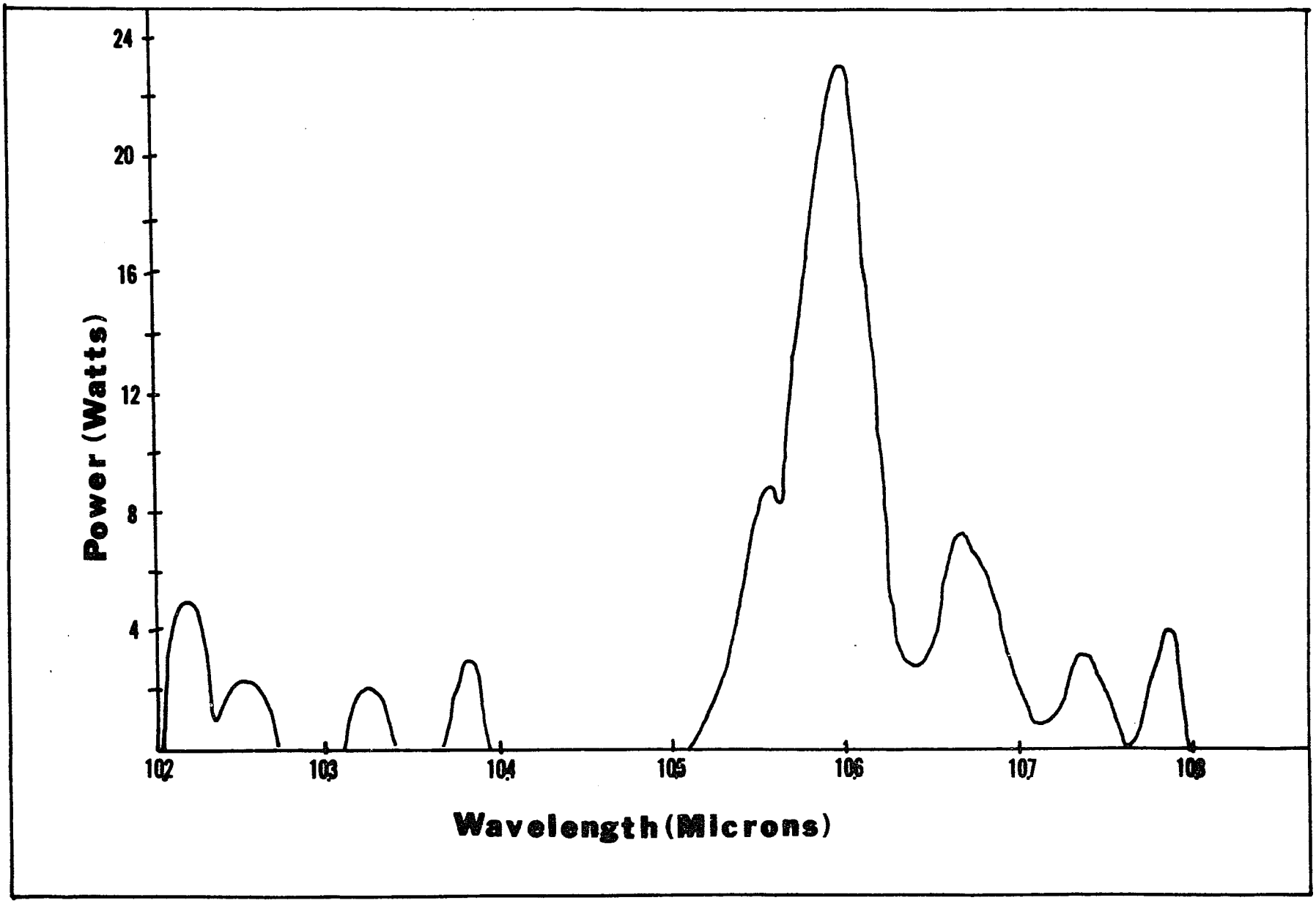
When this study first began, there were a number of problems with the Perkin-Elmer laser. The mount which held the output mirror in place was made of Teflon. When the beam struck a window of IRTRAN II, some of it was reflected back. The studies made before this one all employed cells with this window material. A small percentage of the beam had evidently been reflected back and melted the mount. Some of the molten Teflon had gotten on the mirror and had subsequently burned off. This had left the mirror pitted and probably led to a great deal of dispersion.

While the laser was in this condition, the operating wavelengths were measured. It was found that there were a number of lines from 10.2 microns to 10.8 microns, as shown in Figure 8. The total power output of the laser varied with time. In addition to this, the power of the individual lines varied. The latter variation was much larger than the former; i.e., the ratio of power of one line to another varied.

If the laser was directed at a sheet of asbestos, the spot where the beam struck was heated to incandescence. From this glowing surface, a good idea of the transverse power distribution of the beam could be gained. This distribution is generally called a transverse electric mode (TEM).

Figure 8

PERKIN-ELMER LASER OUTPUT WAVELENGTHS


24
20
16
12
8
4
Power (Watts)
102
103
104
105
106
107
108
Wavelength (Microns)

The pattern on the glowing surface is similar to the far-field patterns taken on photographic film. These patterns are used to check the moding in visible lasers. When the glowing pattern on the asbestos was observed for a time, it could be seen that the laser was changing modes rapidly.

A new mirror was ordered for the Perkin-Elmer laser, and when installed, it seemed to improve it in a number of ways. The main improvement was that it began to "lase" at only three frequencies. These lasing lines were 10.58, 10.60, and 10.62 microns. The power was in a ratio of 1:3:1, respectively.

Figure 9 is an abbreviated energy level diagram showing some of the vibrational states of the carbon dioxide molecule. Under certain conditions, carbon dioxide can be excited to these energy levels in a gas discharge. The state $00^{\circ}1$ is relatively long-lived. Nitrogen can increase the population of this state by collisional transfer of energy. The main mechanisms which lead to population of the $00^{\circ}1$ state are electron impact and collisional transfer from nitrogen. Then, by stimulated emission, the carbon dioxide molecules are brought to either the $10^{\circ}0$ state or the $02^{\circ}0$ state. The molecules in these states must be de-excited before they can be re-excited to the $00^{\circ}1$ state. This is believed to be accomplished in part by the helium, but the main mechanism is thought to be by collisional relaxation between the carbon

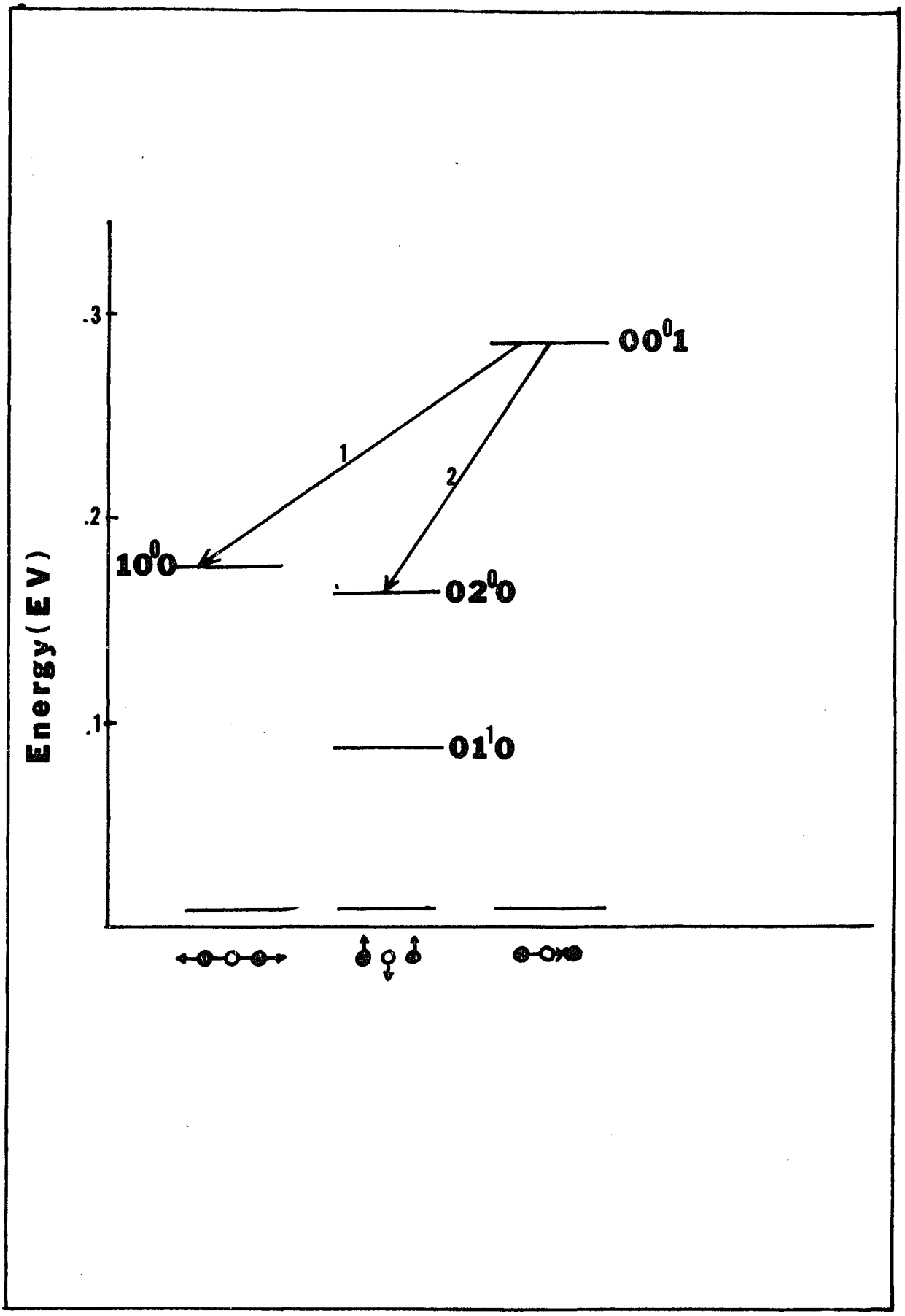
Figure 9

CARBON DIOXIDE VIBRATIONAL ENERGY LEVELS INVOLVED

IN LASER ACTION NEAR 10 MICRONS

1. 10.2 to 10.4 (R Branch)
   10.4 to 10.9 (P Branch)

2. 9.2 to 9.4 (R Branch)
   9.4 to 9.8 (P Branch)


Energy(EV)
.3
.2
.1
$00^0 1$
$10^0 0$
$02^0 0$
$01^1 0$
1
2

dioxide molecules themselves. It is also believed that the vibrational energy is transferred through a number of steps to transitional energy. This de-excitation process is slow compared to the other essential laser processes (e.g., nitrogen excitation, nitrogen to carbon dioxide energy transfer, and stimulated emission), and therefore limits the intensity of the output radiation.

With the above considerations in mind, the tunable laser was built so that the translational energy produced could be carried off. This was accomplished in two ways: (1) a flowing gas system was employed, and (2) the walls of the discharge tube were water-jacketed. These and certain other features made it possible to use most of the system with another set of lasing gases to produce wavelengths outside of the range of carbon dioxide.

The greater the distance between electrodes in a plasma tube is, the higher the voltage must be to maintain a plasma. In the type of a.c. power supply used, the voltage dropped to zero 120 times per second. Since it was desirable to minimize the time that the plasma was off, the electrodes in the plasma tube were placed as close to one another as possible.

On the other hand, the amount of gain obtained from a laser is proportional to the length of the medium in which gain occurs. In this case that medium was the plasma. To

compromise between these conflicting considerations, three electrodes were employed in the plasma tube. This meant that due to the type used, two transformers were employed.

From the above, there arose another problem. Each transformer had two output leads. One lead from each transformer was hooked to the end electrodes. The remaining two leads, (one from each transformer) were combined and hooked to the middle electrode.

The question of phase then arises. Since the transformers are both hooked to the same line source there is a fixed phase-relation between them. Let us label the transformers (a) and (b), and the two leads on each transformer (1) and (2). At some instant in time, lead (1a) will be positive in relation to lead (2a); and at this same instant in time, lead (1b) will be positive in relation to lead (2b).

Therefore, at the instant of time in question (remembering that one lead each will be hooked to the end electrodes and two leads will be combined in the middle), the relationship between the electrodes can be represented by one of the following: (+) (-) (+) or (+) (-+) (-). Which representation applies depends on how the transformers are hooked up.

It was found that the (+) (-) (+) manner gave the more stable plasma and, therefore, more gain. This transformer configuration was used thereafter.

It was observed that the discharge at the electrodes was irregular; also, there seemed to be some discharge from within the electrode rather than just on the rim surface. The discharge, instead of being evenly distributed on the rim surface, seemed to be coming from a number of small spots, causing pitting in the surface of the aluminum. To correct this, the electrodes were carefully sanded, polished and buffed. Then, the inside surfaces of the electrodes were sprayed with Teflon coating material and "cured" in an oven at 100 degrees Centigrade for about four hours. When the electrodes were replaced in the laser, it was observed that the discharge was even, and came only from the rim surface.

To get the laser aligned and working, a flat rear mirror was used. This mirror was made by vacuum-depositing gold on the surface of a two-inch optical flat which was purchased from Oriel Optics. In the same bell jar batch, a hold-coupled mirror (the use of which will be discussed later) was also deposited. These mirrors were coated with about 600 angstroms of gold. (A copper mirror was also made by coating a two-inch flat.)

The fabrication of partially-reflecting output mirrors was also attempted. This was done by depositing varying thicknesses of gold on an IRTRAN II substrate.

The mirrors made in this manner had transmission percentages of 60, 40, 25, 20, and 15. These were measured

at 10.6 microns with an identical piece of IRTRAN II in the reference beam of the infrared spectrophotometer which was used. The one which worked best was the twenty per cent transmission, but its power output was an order of magnitude below that of the commercial mirrors.

Besides the low power output, these mirrors of gold-coated IRTRAN II exhibited very complicated transverse mode patterns. One problem was obvious--the transmission, not the reflection, was being measured. The decrease in transmission could have come from both scattering and reflection. The mirror-making project was abandoned.

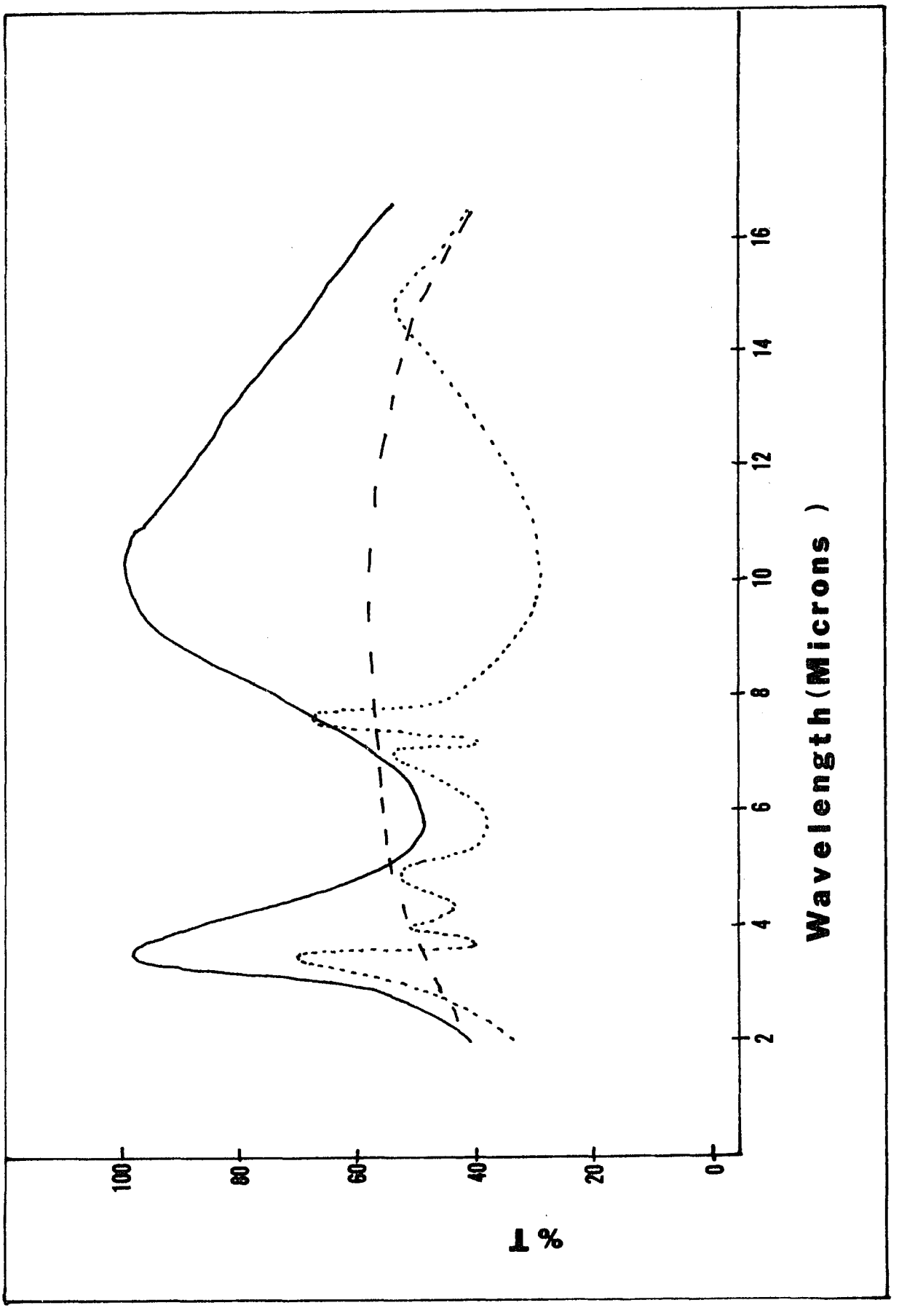
The commercial mirror used was twenty per cent reflecting on one surface and antireflection-coated on the other. The question then arose of which surface should be facing the plasma. Because the substrate was so highly transmitting at the laser wavelengths (Figure 10) and was antireflection-coated (the refractive index of germanium at 10.6 microns is four), it should not have mattered. The surfaces were not labeled in any way, although there was some difference discernable to the eye. As it happened though, the laser would not work with the mirror in one direction, but would work with it in the other. No explanation has been found for this.

The windows of the plasma tube were not placed at the Brewster angle for three reasons. First, since the laser

Figure 10

GERMANIUM ABSORPTION SPECTRUM

Solid Line: Antireflection-Coated Window
Dashed Line: Uncoated Window
Dotted Line: 20% Reflecting Output Mirror


100
80
60
40
20
0
% T
2
4
6
8
10
12
14
16
Wavelength (Microns)

beam would already be polarized by the grating, the alignment problems inherent with Brewster angle windows would be multiplied. Second, because the index of refraction of germanium at the laser wavelength is so high, and because the tangent of the Brewster angle equals the index of refraction;[31]

$$\tan \theta_B = N$$

$$\tan \theta_B = 4$$

$$\theta_B = 76 \text{ degrees}$$

$$\cos \theta_B = \text{beam diameter/diameter of window}$$

$$0.24 = 1/D_w$$

$$D_w = 4.2 \text{ inches}$$

therefore, 4.2 inches of germanium would have to be used. Four inches is rather large for a germanium window. Third, it was hoped that the laser would eventually be made into a bellows-sealed system requiring no windows.

Sodium chloride windows were tried in place of the germanium and seemed to be comparable, but due to the salt's inherent moisture problems, these were not routinely used.

As it was first built, the laser put out only about three watts maximum. This was without the grating which would reduce the power some sixty per cent further. This was very disappointing so further modifications were made.

It was decided that the discharge may have been at fault and this was due to the design of the electrodes. Some

commercial electrodes suitable for glass enclosure were purchased. These electrodes had a small bead of uranium glass on the wire leading to them which would seal with Pyrex glass. Three electrodes were built--two end electrodes and one middle electrode. The design of these is shown in Figure 11.

The end electrodes were simply placed between the aluminum end pieces and the water-cooled cavity, but the center electrode replaced the middle aluminum piece. These electrodes were made out of pyrex and had 29/42 standard taper joints on them.

The standard taper Teflon sleeves were always used instead of grease because it was found that even a very small amount of grease vapor spoiled the plasma.

The next modification was the elimination of one window. By sealing the plasma tube with the output mirror, it was expected that one source of loss would be eliminated. The problem with this was that this mirror would no longer be adjustable. If bellows were used between the plasma tube and the mirror mount, both sealing and adjustability could be obtained. The bellows mount is shown in Figure 12.

It was found that the springs in the Oriel mirror mount were not strong enough to deform the bellows during adjustment. Because of the size of the mount, it was impossible to put in a larger spring, so another mount was designed and is shown in Figure 13.

Figure 11

GLASS ENCLOSED ELECTRODES

A. End Electrode
B. Middle Electrode

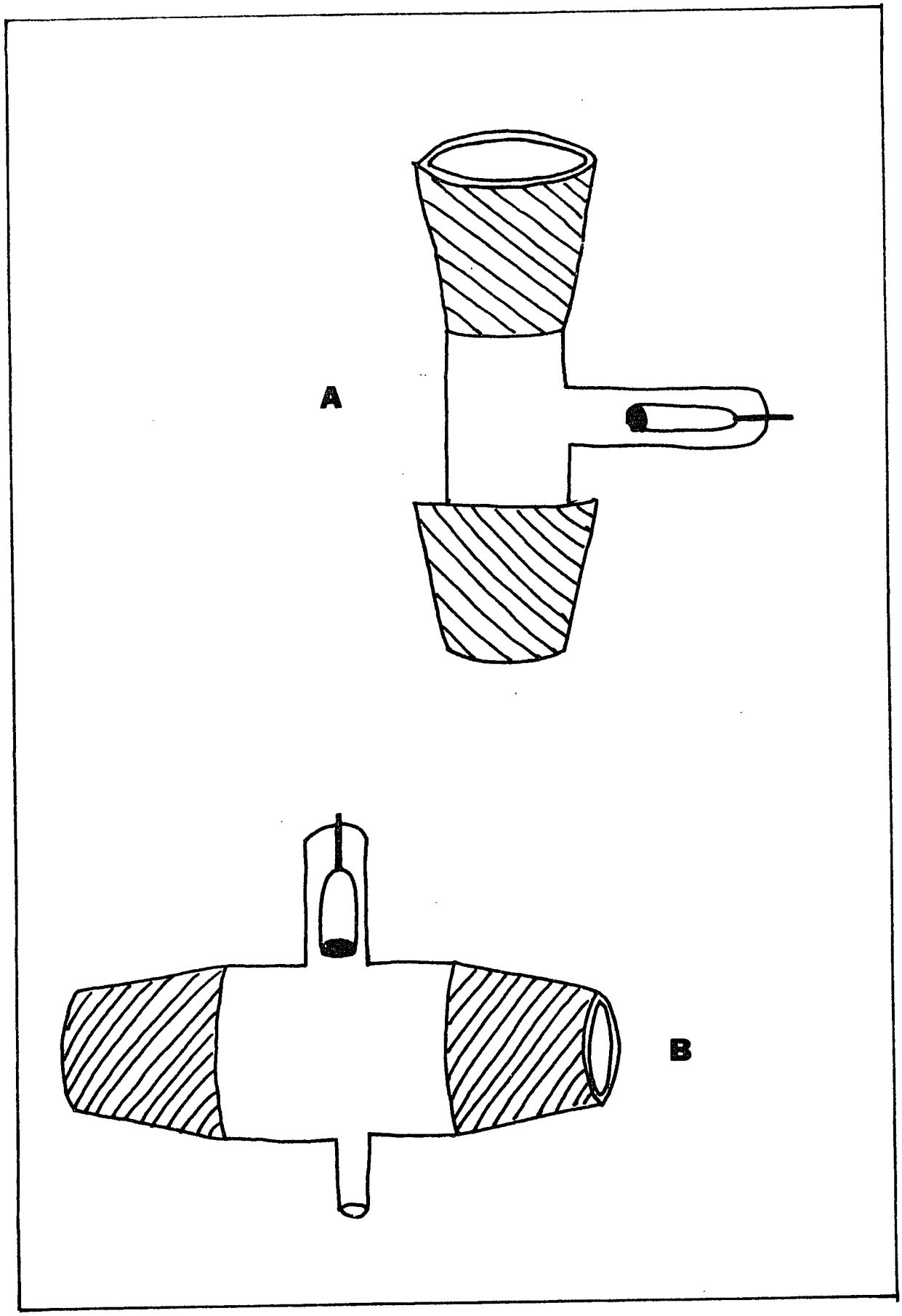

A
B

Figure 12

BELLOWS MIRROR MOUNT

1. Teflon
2. P.V.C. Mirror Retainer
3. Mirror
4. "O" Ring
5. Brass Mirror Holder
6. Clamping Ring

(Bench Mount is Clamped Between 1 & 6)

7. Swagelok Steel Bellows

(The rest of the mount is similar to Figure 4)

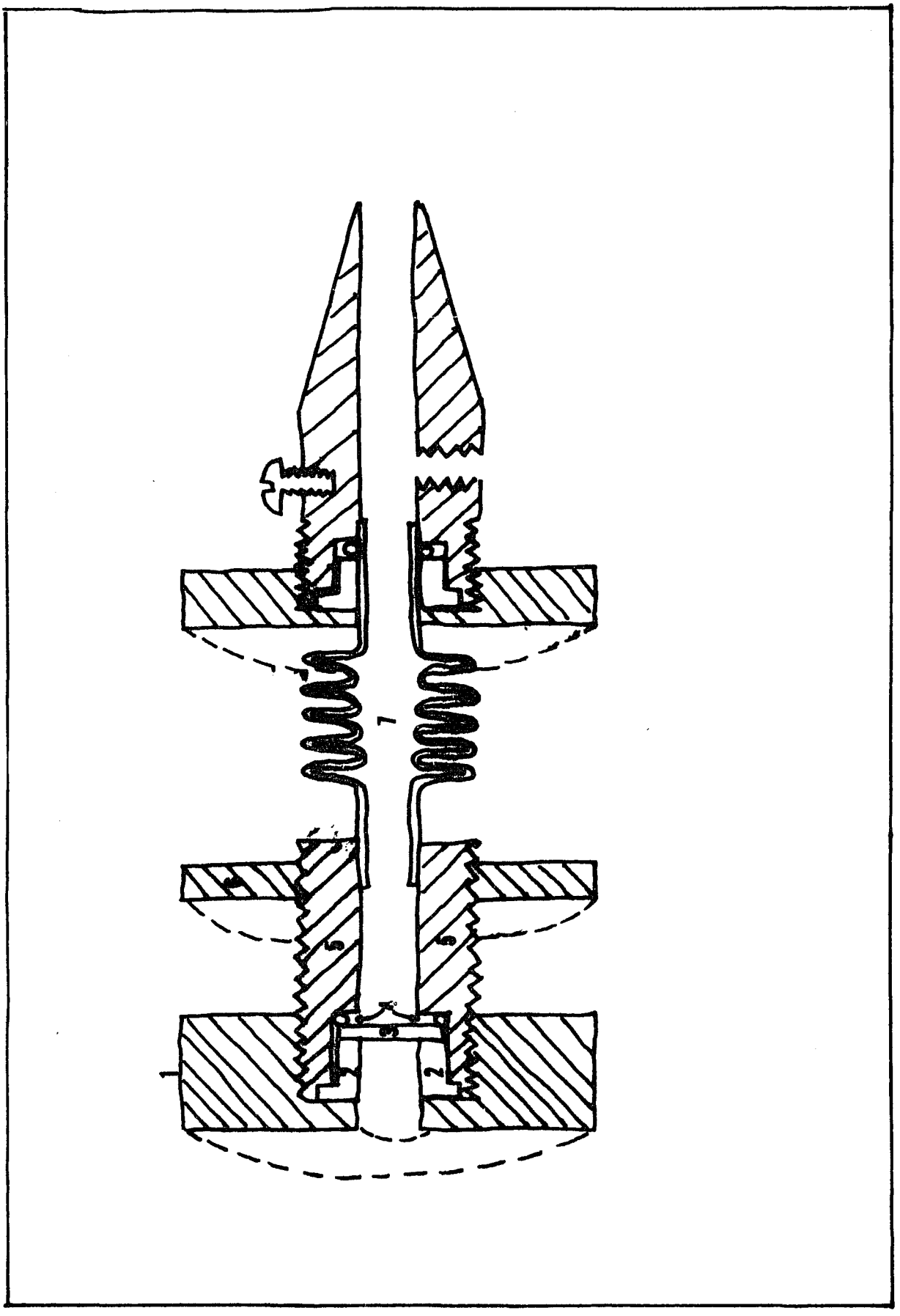
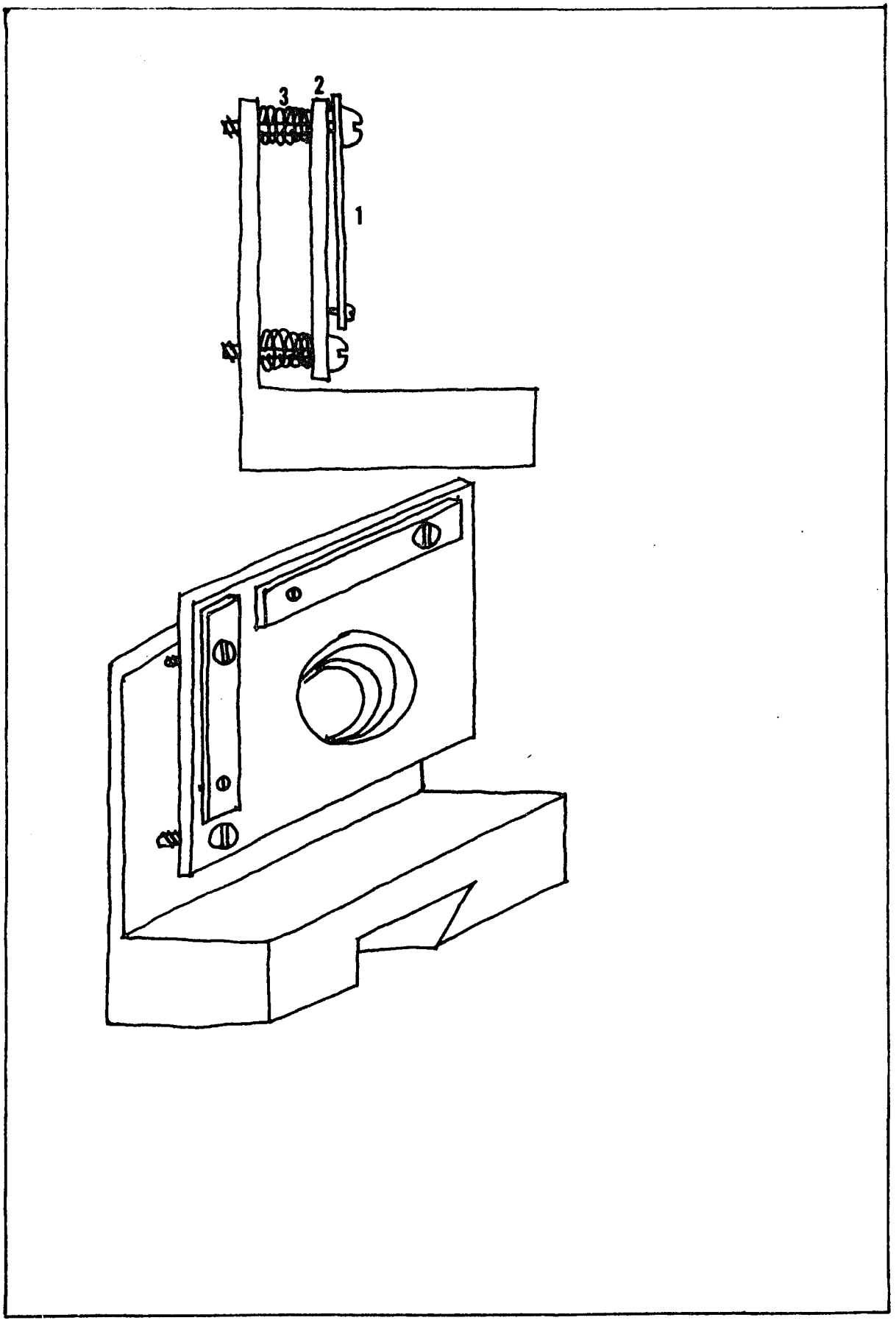

7
5
6
3
2

Figure 13

BENCH MOUNT FOR BELLOWS MIRROR MOUNT

1. Lever Arms for Fine Adjustment
2. Plate Which is Caught Between Parts 1 and 6 of Figure 12
3. Heavy Duty Springs


3
2
1

Because of the fact that the grating must be sealed at an angle and the adjustment must be moved through a larger arc than the output mirror, this modification is yet to be accomplished.

The laser parts were lined up on the optical bench by using the helium-neon laser. First the helium-neon laser was aimed so that it was horizontal. This was done by aligning the laser with a bubble-type level. The beam had to be a convenient height above the laboratory table top so that the optical rail and the laser components could be easily aligned. The optical rail was made level by using a rod machined to a point and placed in a rail mount. This point was aligned so that its tip was just touching the beam when it was at one end of the rail. Then, the rail was aligned so the tip was just touching the beam when the mount was moved up and down the rail.

The glass, water-cooled plasma-tube parts were aligned so that the beam passed through the exact center of each. The electrodes and end aluminum pieces were then placed on the plasma tube parts.

When a rear mirror was used, it was lined up first so that the incident beam from the helium-neon laser hit it in the center and the reflected beam went back and struck the front of the output mirror of the helium-neon laser. This then gave a reflected beam which struck the rear mirror of

the disassembled carbon dioxide laser. This was reflected back toward the helium-neon laser, etc. In this manner, very good perpendicular alignment of any reflecting surface to the helium-neon laser beam was achieved.

The front mirror (output) was aligned in the same manner, subsequent to the placement and alignment of all the other laser-cavity parts. When the grating was used as a rear mirror, the procedure was more complicated.

The first thing to do was to line the grating up so that the rulings were vertical. The grating was rotated by hand with the helium-neon laser beam falling on it. After each rotation of the grating, the horizontal adjustment on the grating mount was moved and the reflected spots were observed. When the reflected spots were observed to sweep completely horizontally, the rulings were completely vertical. When the reflected spots were observed to sweep across the output mirror of the helium-neon laser, the grating was vertically aligned.

The next problem was getting the system to "lase". Using the helium-neon laser again, it was reasoned that around the seventeenth order of the 6943 angstrom line, reflected back on itself from the grating, should give the first order 10.6 micron wavelength. This was never successful. So many orders were observed that the seventeenth could not be picked out. There were spots in the whole 180 degree range in front

of the grating. There were two spots, however, which were much brighter than the others. It was reasoned that since the grating was blazed for 10.6 microns, these spots must correspond to approximately the seventeenth order. This was not successful either.

The grating was finally aligned by trial and error. The flat output mirror was replaced with a window, and a hole-coupled mirror was used as a front mirror. Hole-coupled mirrors are concave mirrors with small holes in their center. The radius of curvature of this one was about ten meters. Because of this, alignment of this mirror was much less critical.

"Lasing" was obtained with this mirror and the grating and then the output was maximized. Then the flat output mirror was put back in and this alignment was maximized.

In this configuration, the laser could be tuned through all lasing wavelengths by just using the coarse horizontal adjustment. A maximum of twenty watts was obtained with the grating. This corresponds to a fifty watt, plane-mirror output. The output wavelengths versus power are shown in Figure 14.

Before the final maximization of alignment, a maximization of the concentration of the lasing gases was done. For a long while after the laser was first assembled, no lasing could be obtained even after very careful alignment.

Figure 14

OUTPUT WAVELENGTHS OF THE TUNABLE LASER

VERSUS WAVELENGTH (LOW RESOLUTION)

Power (Watts)
2
4
6
8
10
90
92
94
96
98
100
102
104
106
108
Wavelength (μ's)

It was noted that the color of the discharge was different from that of the Perkin-Elmer laser. This was the only clue to go on, because when there is a zero power there can be no maximization. It was believed that the flow rate was too low and the plasma pressure too high to permit lasing. The vacuum-metering and shutoff valves were removed and all the tubing outside the flow module was changed to one-half inch polyethylene. After this was done, lasing was finally obtained.

Then, studies aimed at producing maximization through gas concentration changes were done. These studies were made before the power meter had arrived. The relative power was measured by using a cone of brass foil (height approximately 0.5 inch, and base diameter approximately 1.0 inch), to which was attached a thermocouple. The voltage output of the thermocouple was measured on a Hewlett-Packard Model 425-A microvoltammeter.

The parameter which was measured in these studies was the flow rate of each gas. This was monitored between the plasma tube and the vacuum pump with a thermocouple gauge attached to a brass "T". This type of study was done after each modification of the laser. The data from the final study is shown in Figures 15, 16, 17, and 18.

Also, a study of the input voltage versus the output power was done for both the 30 milliamp and the 120 milliamp transformers. The results are shown in Figure 19.

Figure 15

CARBON DIOXIDE FLOW RATE VERSUS POWER

(With Nitrogen and Helium Flow Rates Maximized)

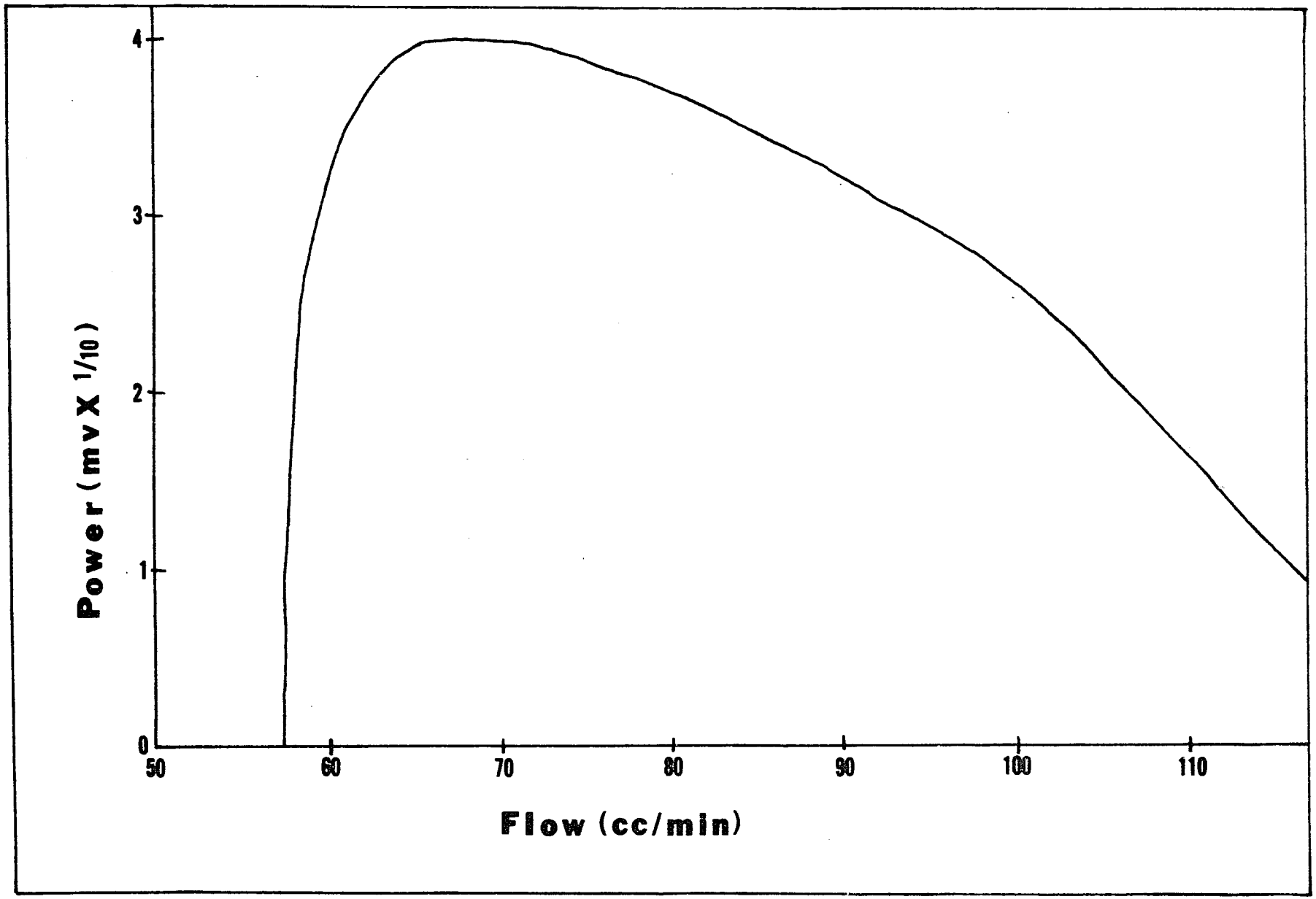

Power (mv X 1/10)
4
3
2
1
0
50
60
70
80
90
100
110
Flow (cc/min)

Figure 16

NITROGEN FLOW RATE VERSUS POWER

(With Carbon Dioxide and Helium Flow Rates Maximized)

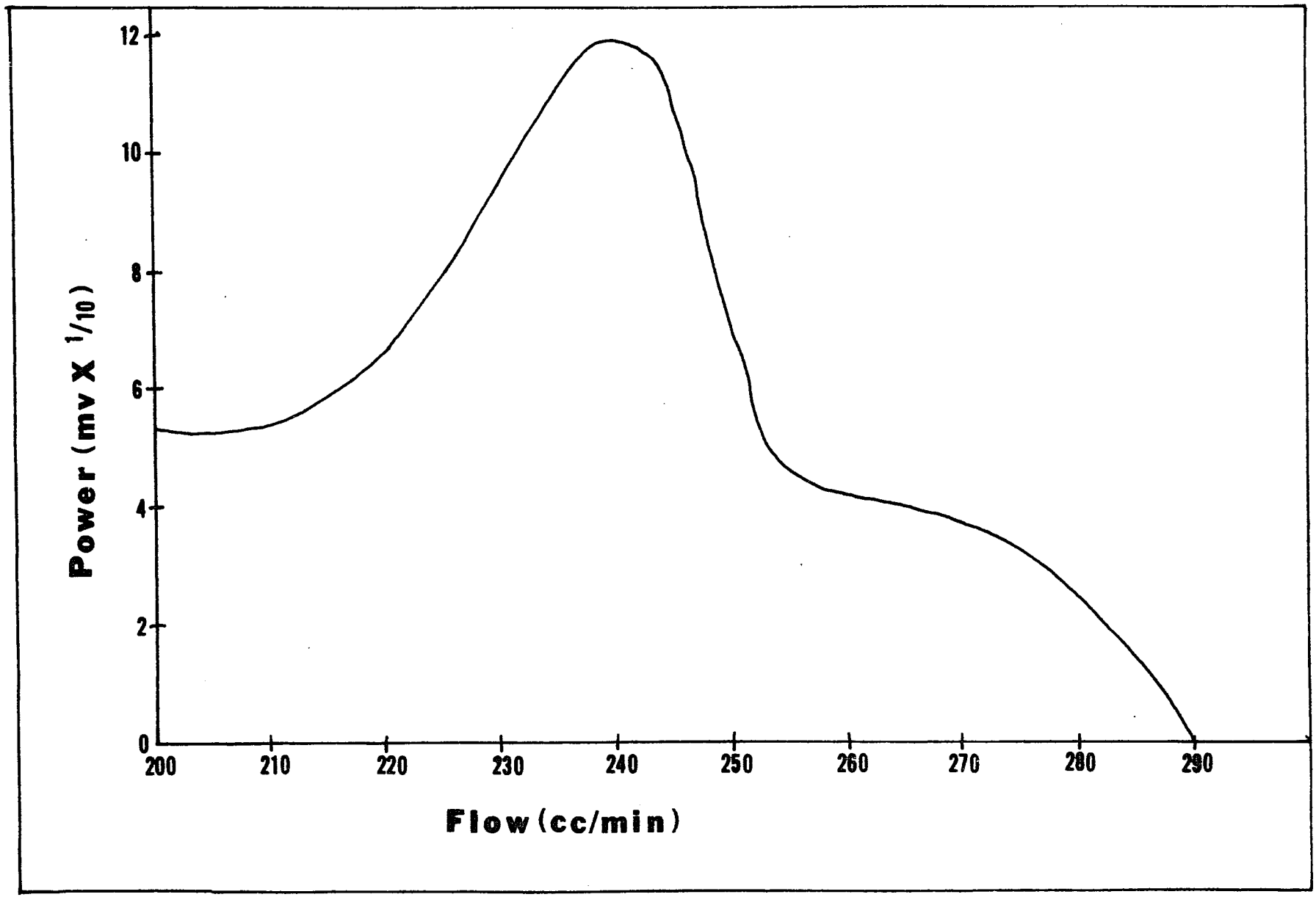

Power (mv X 1/10)
12
10
8
6
4
2
0
200
210
220
230
240
250
260
270
280
290
Flow (cc/min)

Figure 17

HELIUM FLOW RATE VERSUS POWER

(With Carbon Dioxide and Nitrogen Flow Rates Maximized)

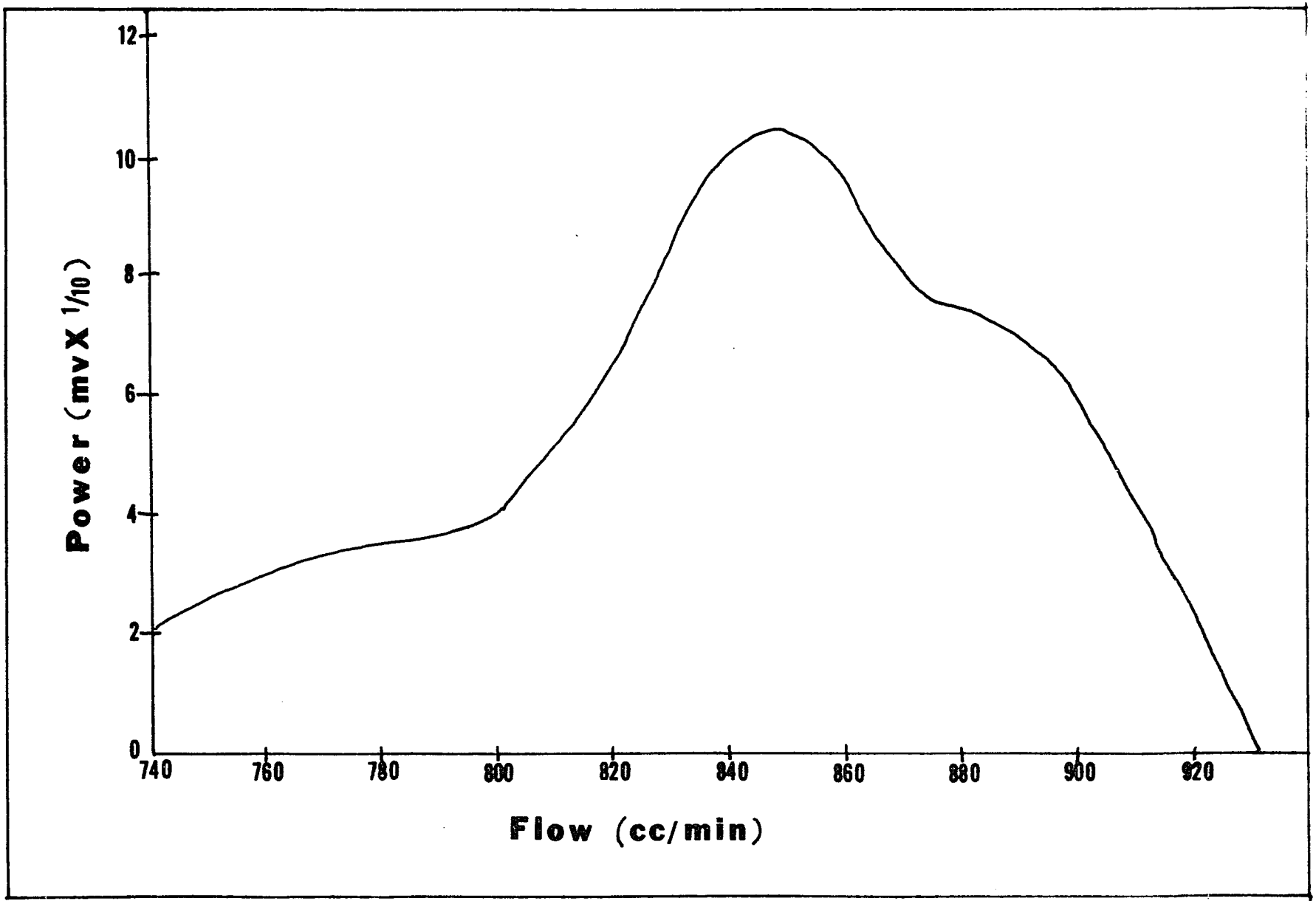

Power (mvX 1/10)
12
10
8
6
4
2
0
740
760
780
800
820
840
860
880
900
920
Flow (cc/min)

Figure 18

TOTAL FLOW RATE VERSUS POWER

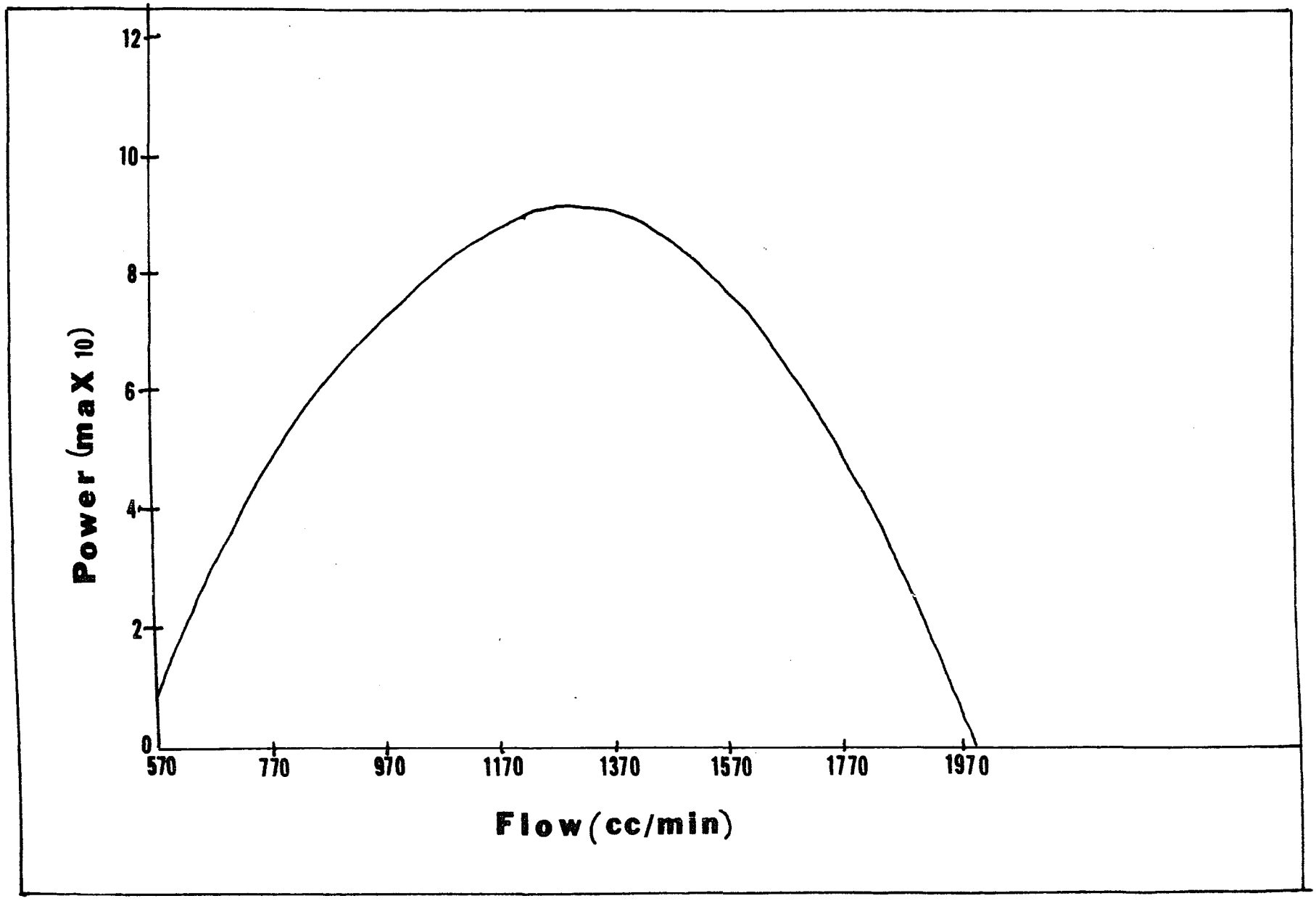
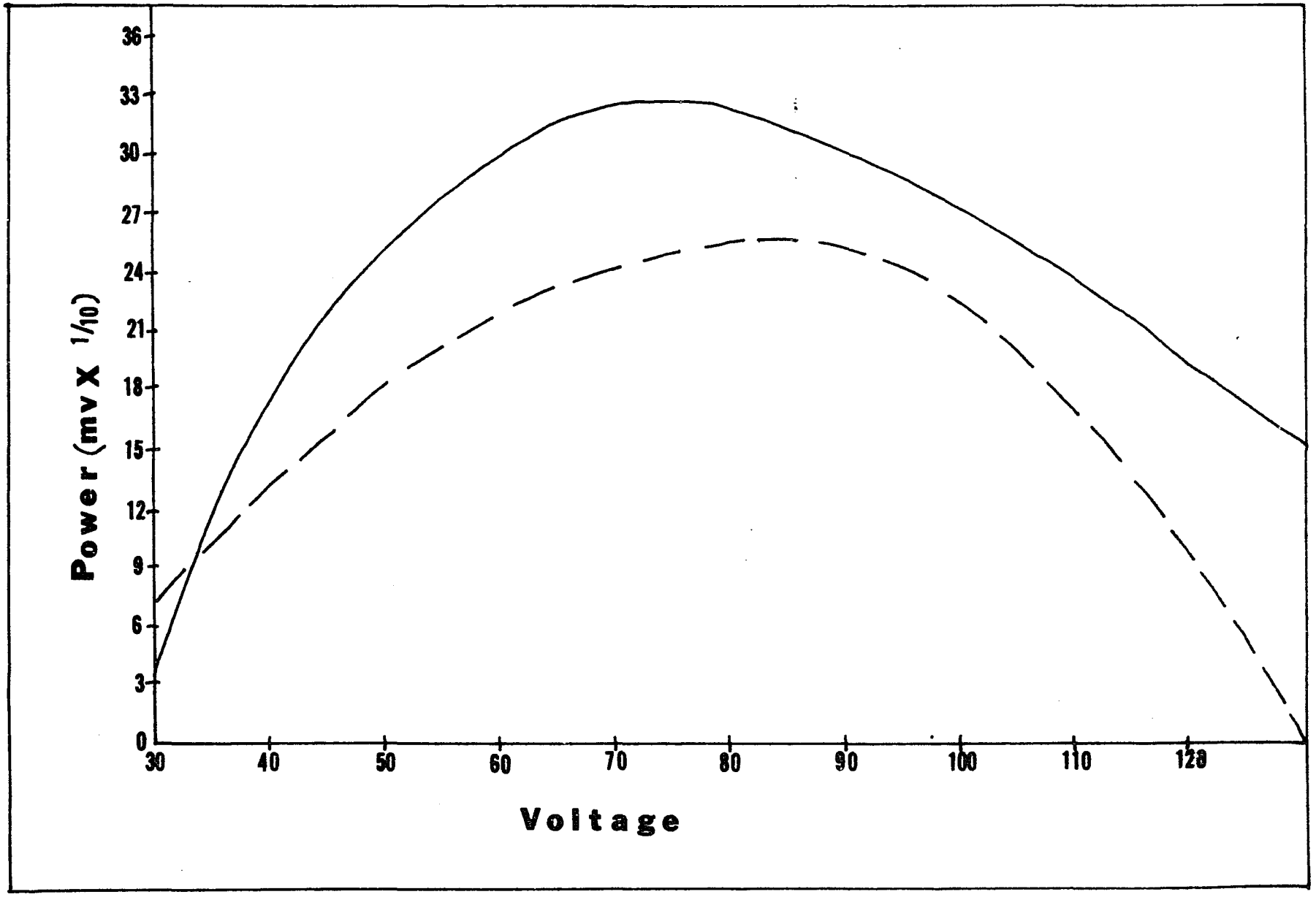

12
10
8
6
4
2
0
Power (maX 10)
570
770
970
1170
1370
1570
1770
1970
Flow (cc/min)

Figure 19

VOLTAGE SUPPLIED TO PLASMA TUBE VERSUS POWER

Solid Line: 30 milliamp transformers
Dashed Line: 120 milliamp transformers


Power (mv X 1/10)
36
33
30
27
24
21
18
15
12
9
6
3
0
30
40
50
60
70
80
90
100
110
120
Voltage

It was seen that no more power was obtained when the 120 milliamp transformers were used. Furthermore, it was seen that a more definite maximum in the power curve was reached in the case of the 120 milliamp transformer. It was also observed that electrode heating, which hithertofore had been controlled adequately through use of directional air streams, became more of a problem. Due to this, the 30 milliamp transformers were used for the laser power supply for the rest of the study.

This seemed to indicate that the lower ($10^{\circ}0$ and $02^{\circ}0$) lasing states were not being depopulated to the ground state quickly enough. There was no way to increase the flow rate, but the tap water was observed to be about thirty degrees Centigrade, so the water jacket definitely could be cooler. A water refrigeration unit with antifreeze was employed to decrease the temperature of the jacket to very near the freezing point of the mixture (0 degrees Farenheit); however, this did not increase the power detectably, so the refrigeration system was abandoned.

It was observed that sometimes there was a drastic decrease in the output power of the laser. This was observed to be accompanied by a flickering of the plasma. When the mirror or window nearest the source of the flickering was removed, it invariably had a greasy substance on its surface. It was concluded that this material must have been from the "O" rings or from the window mounts. When removed, the "O"

rings were observed to be cracked and discolored. When "O" rings with a larger inside diameter were put in, this flickering, with accompanying power decreases stopped.

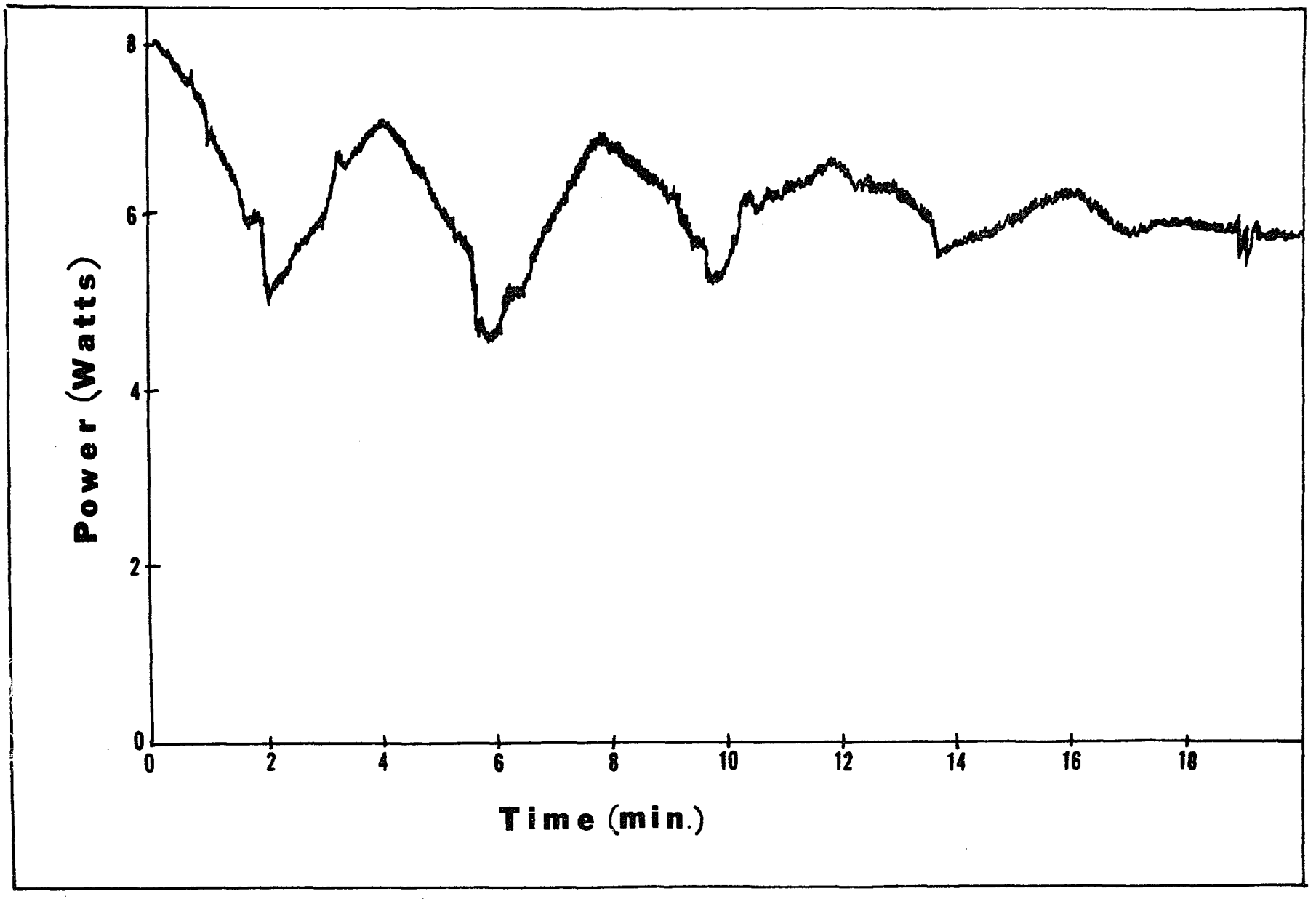
When the laser power was observed over a period of time, an unusual effect was noticed. The power varied almost sinusoidly with time. The average frequency of this "sine wave" was about three minutes. It the laser was allowed to warm up for about fifteen minutes, it would stabilize as if some equilibrium had been reached. This is shown in Figure 20. When a Sola "Filter" transformer was placed in the power supply circuit, it did not help. There are three observed effects which might have had a bearing on the above.

First, the grating mount had a translational micrometer adjustment on it. This adjustment made the laser cavity (not the plasma tube) longer or shorter by small amounts. When the adjustment was turned, the power of the laser was observed to rise and fall. Attempts were made to study this effect quantitatively; i.e., to study laser power in relation to changes in cavity length. The results were erratic and irreproducable, probably due to the fact that the system had to equilibrate during each adjustment.

Second, it was observed that the output mirror was heating up. The mirror housing and "O" ring holding-insert were made of polyvinyl chloride. New pieces were made of brass to help carry off the heat.

Figure 20

LASER POWER VERSUS TIME


Power (Watts)
0
2
4
6
8
0
2
4
6
8
10
12
14
16
18
Time (min.)

Third, the grating and grating mount were observed to be heating up also. The heating was observed to reach what seemed to be an equilibrium.

It would seem that probably these heating effects and the longitudinal tuning effect might have been combining to give the sinusoidal power variation which was observed. Some piece or pieces were heating, and therefore expanding, until thermal equilibrium was established.

To see if a plasma tube more like that of the Perkin-Elmer would increase the power of the system, an air-cooled plasma tube was made. Gold was vacuum-deposited on a one-inch optical flat. This was used as the rear mirror in the air-cooled plasma tube. For a front (or output) mirror, the eighty per cent transmissive, antireflection-coated germanium mirror was used. A bellows "O" ring system was used to seal to the ends of the glass tube. This was done at both ends. Figure 21 shows how this was done.

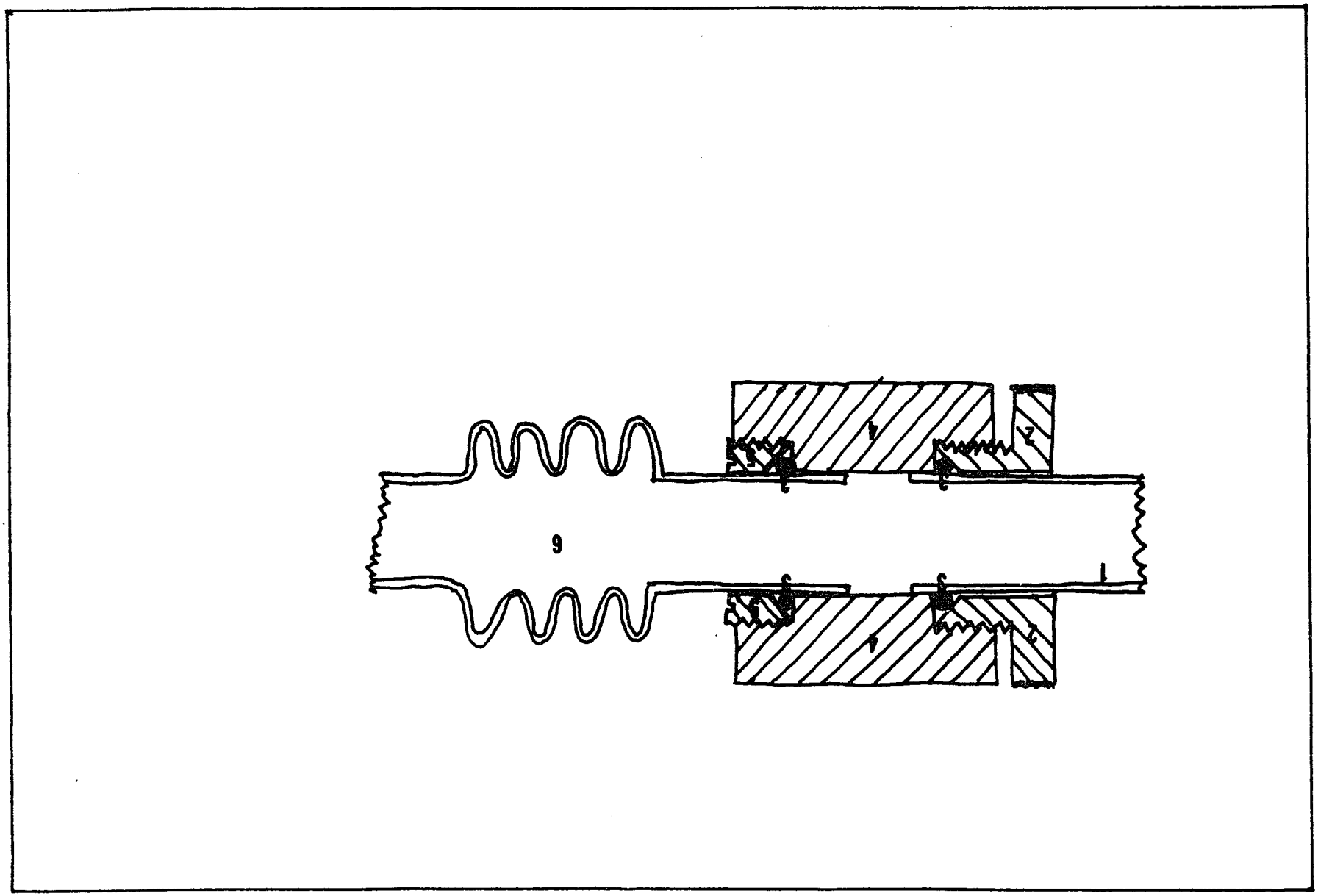
The system was "peaked up" by maximizing the three gas concentrations, and by adjusting the mirrors in relation to one another. When all this was done, the maximum power was about eight watts. The rear mirror was then removed and a window was put in its place.

The grating was then set in place and was used as the rear mirror. This configuration only gave about three to four watts maximum. The air-cooled tube was then abandoned.

Figure 21

GLASS TUBE TO BELLOWS "O" RING SEALED CONNECTOR

1. Glass Laser Tube (Truncated)
2. Knerled "O" Ring Depressor (Teflon)
3. "O" Ring
4. Main Connector Body (Teflon)
5. "O" Ring Depressor with Holes (2) for Wrench
6. Bellows (Truncated)


9
1
2
2

Attempts were made to Q-switch the laser to see if a substantial increase in power could be obtained. A special chopper blade was made for this purpose. It was about seven inches in radius with two one-inch holes drilled 180 degrees from one another.

The blade was placed in the space between the grating and the plasma tube. The blade was rotated at the maximum chopper speed of 83 Hz. While the blade blocked lasing, the population of the $00^{\circ}1$ state built up past its equilibrium value, so that when a hole came around a large pulse was generated. The average power was decreased by an order of magnitude by using the chopper in this manner.

The scattering intensity (off a piece of IRTRAN II) of the "Q-switched" laser showed only a fourfold increase over the scattering intensity of the laser when the beam was chopped between the laser and the scatterer.

It was decided that this increase did not offset the decrease in average power, and the synchronization difficulties which Q-switching would eventually bring about.

MIRROR DEPOSITION

A diagram of the apparatus used in vacuum deposition is shown in Figure 22.

There were a number of problems involved. The piece to be coated and the gold (supported by a tungsten ribbon) were placed inside a bell jar and evacuated to 10^{-5} torr. A current of about five amps was then passed through the ribbon causing it to heat to incandescence.

Problems with the transformer in the apparatus precluded any more than five amps being drawn. Because of this, the usual method of getting a coating of a certain thickness was not used.

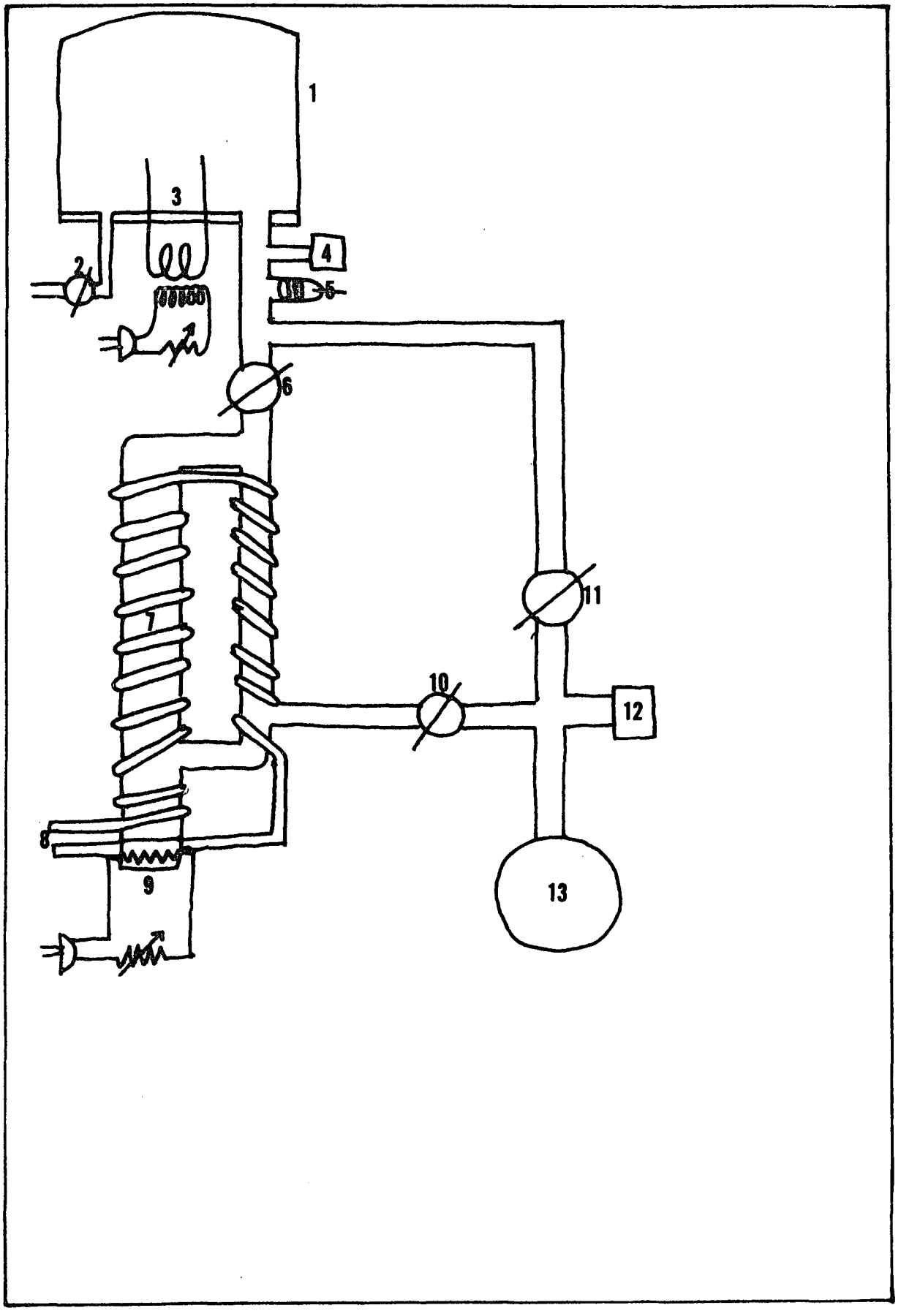
This method is to weigh out the gold and evaporate it entirely. By varying the amount of gold placed in the apparatus, the thickness of the coat is varied and can be standardized.

Instead, the tungsten ribbon was coated with gold by placing a large amount of gold on the ribbon and slowly melting the gold until the surface of the ribbon was wetted evenly. Then the time during which the current was flowing through the ribbon was varied, thereby varying the coat thickness.

Figure 22

VACUUM DEPOSITION APPARATUS

1. Glass Bell Jar
2. "Bleed" Valve
3. Filament Heater
4. Thermocouple Gauge
5. Ionization Gauge
6. Main High Vacuum Valve
7. Oil Diffusion Pump
8. Cooling Water Tubing
9. Oil Heater
10. Diffusion Pump Valve
11. Roughing Pump Valve
12. Thermocouple Gauge
13. Vacuum Pump


1
2
3
4
5
6
7
8
9
10
11
12
13

DETECTION SYSTEM PARAMETERS

The Cassegrainian system cell underwent a number of changes during the course of the experiment. Referring to Figure 7, it is seen that the secondary mirror was a diverging mirror. When this secondary was used, the system focused on infinity. It was found that this configuration gave very little enhancement over a simple, mirrorless cell. This was determined both emperically and by using a small light bult as a source of visible light. The secondary convex mirror was then replaced with a plane mirror. By adjusting the distance between the secondary and primary mirrors, the system was made to focus on a predetermined point along the laser beam inside the confines of the cell, and then onto the slits of the monochromator.

In order to collect more of the fluorescence, it was decided to make the laser beam pass through the hole in the primary mirror. In this way, the system would look along the entire path of the laser beam inside the cell.

It was found that both of these configurations suffered from three problems.

The first problem was that the depth of focus of the system was very shallow. The system collected very little light other than that coming from the small volume upon which

it was focused. In this respect it was no better than the short, mirrorless cells used.

The second problem was that the system "saw" the light scattered from the back window (exit window) and the housing around the cell. This gave rise to a "scatter peak", even when the cell was purged with various clean gases (compressed air, nitrogen, helium, and oxygen). This meant that any resonance fluorescence signal that was to be detected must be detected above the scatter signal. The scatter signal was decreased but was not removed when antireflection-coated germanium windows replaced the IRTRAN II. The scatter signal was removed when the rear plate was removed and a reflecting surface was placed at such an angle that the reflected beam did not go back into the cell.

The third problem was self-absorption. The fluorescence collected by the system and focused onto the slits of the monochromator had to pass through rather large volumes of unexcited gas where it would be reabsorbed. A better system would be one wherein the collection mirrors were located external to the cell, or one which was efficient enough to where very low concentrations could be used.

When the monochromator was first purchased, it had a 150 groove per millimeter grating blazed for six microns. Because of the scanning gear train, this system's maximum wavelength was eight microns. This grating was useful for shorter wavelengths, but was not used in this study.

A 30 groove per millimeter grating blazed for thirty microns was also used. When used without an order-sorter, a scan of an infrared source at about 800 degrees Centigrade is shown in Figure 23. The calculated blackbody curve for such a source is shown in Figure 24. This curve was calculated using Planck's Law:

$$F_\lambda(T,\lambda)d\lambda = \frac{2\pi hc^2}{\lambda^5} \frac{d\lambda}{e^{ch/\lambda kT}-1}$$

The spectrum in Figure 23 was due to the fact that at wavelengths which were an order of thirty microns, there was a higher efficiency than at those which were not.

With the 75 groove per millimeter grating, the order-sorter worked very well. The absorption curves for the various order-sorter filters are shown in Figure 25.

The grating was blazed for eight microns, so the wavelengths from 2.3 microns to 3.5 microns were scanned with Filter Two. The wavelengths from 3.5 microns to 7 microns were scanned using Filter Three, and those from 7 microns to 14 microns were scanned with Filter Four. Such a scan for the 800 degree Centigrade blackbody is shown in Figure 26.

All monochromator emission and absorption studies used the 75 groove per millimeter grating and the order-sorter.

When the Barnes detector arrived, it had been placed in a mount by McPherson. It could be bolted onto the monochromator with no modification. The circuit suggested by Barnes is shown in Figure 27.

Figure 23

SCAN OF INFRARED SOURCE

USING 30 GROOVE PER MILLIMETER GRATING

AND NO ORDER-SORTER

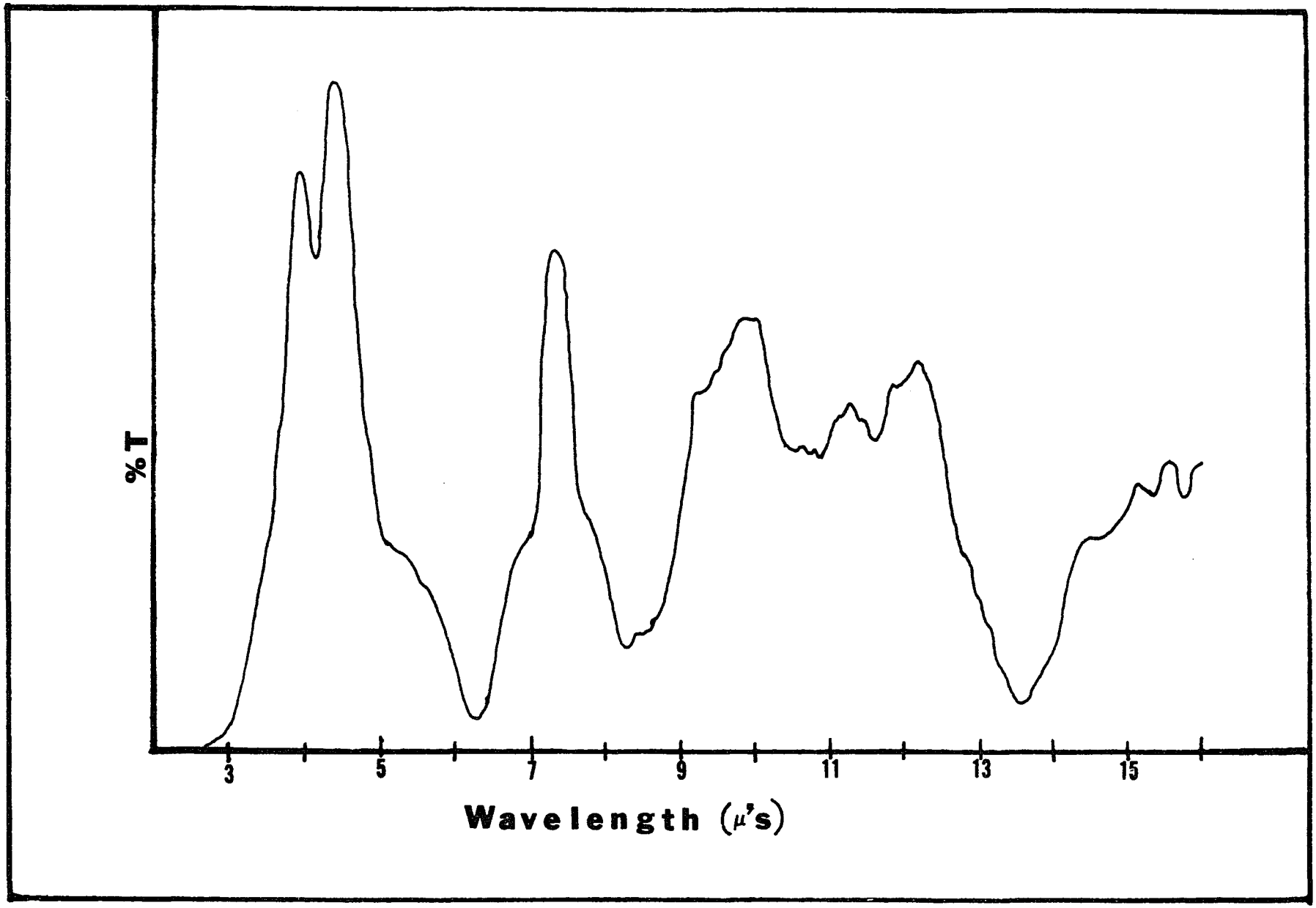

%T
3
5
7
9
11
13
15
Wavelength (μ's)

Figure 24

CALCULATED EMISSION CURVE FOR BLACKBODY

AT 800 DEGREES CENTIGRADE

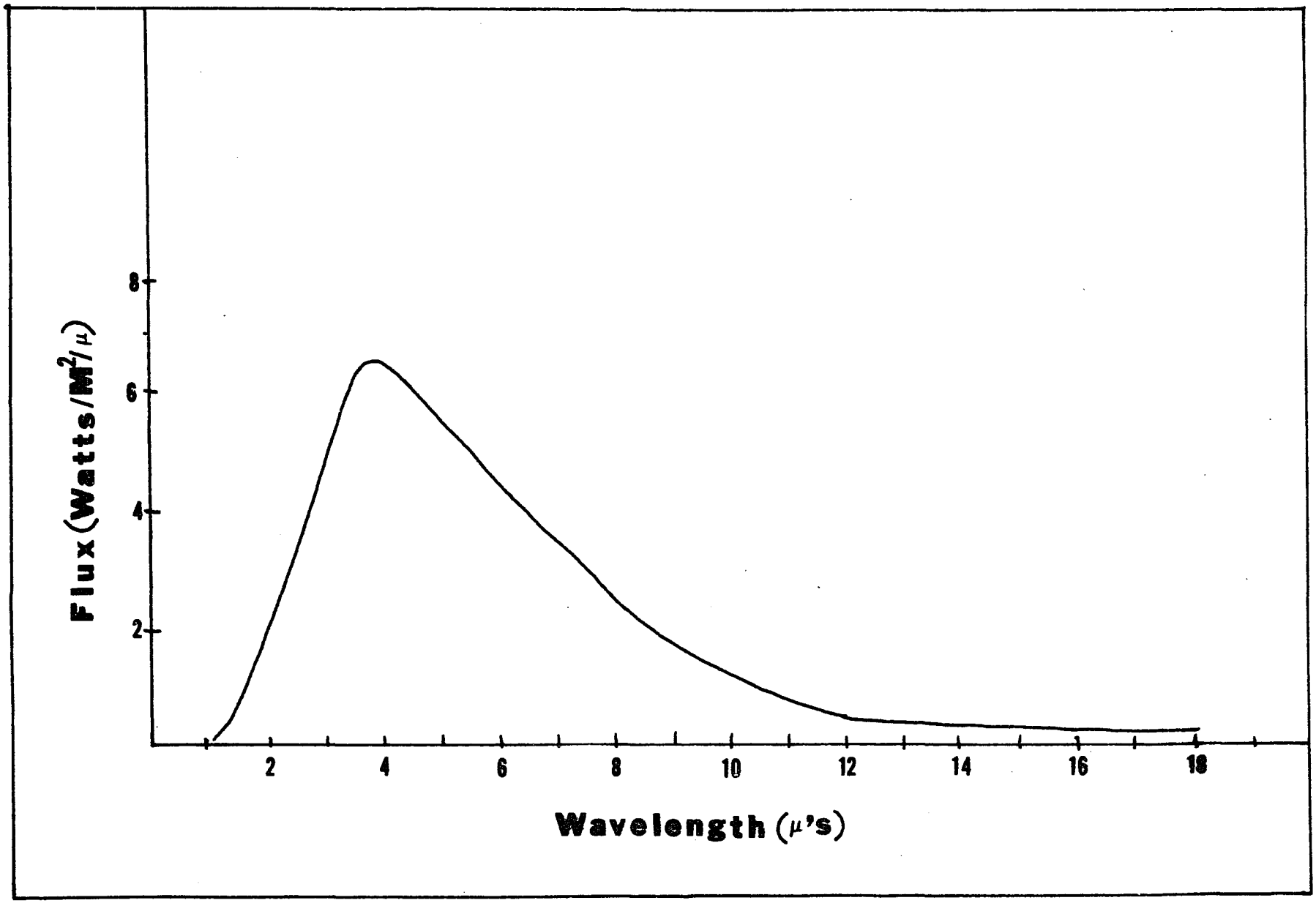

Flux (Watts/M²/μ)
8
6
4
2
2
4
6
8
10
12
14
16
18
Wavelength (μ's)

Figure 25

ORDER-SORTER ABSORPTION CURVES

Solid Line: Filter 2
Dashed Line: Filter 3
Dotted Line: Filter 4

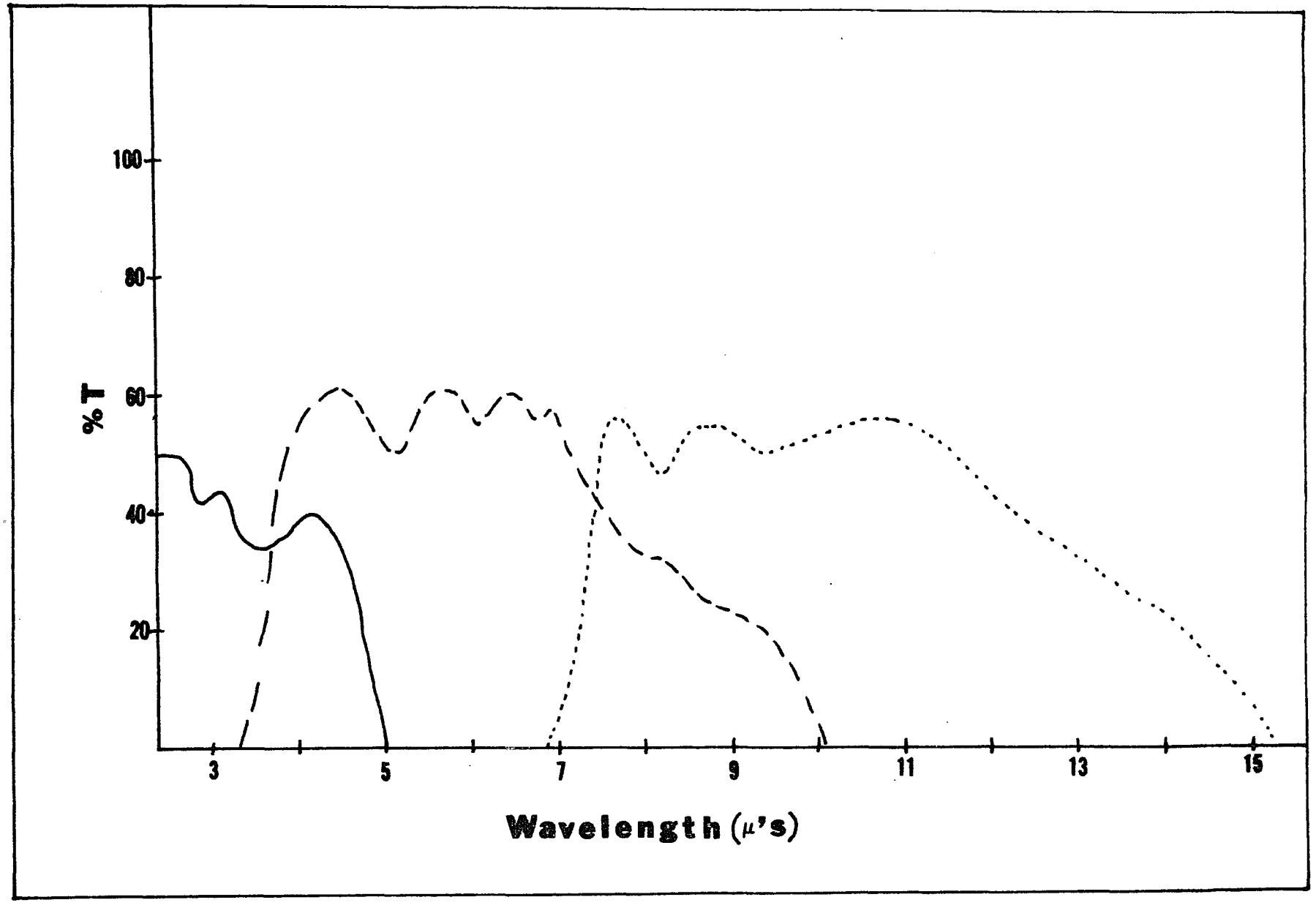

100
80
60
40
20
%T
3
5
7
9
11
13
15
Wavelength (μ's)

Figure 26

SCAN OF BLACKBODY SOURCE

USING 75 GROOVE PER MILLIMETER GRATING

AND ORDER-SORTER

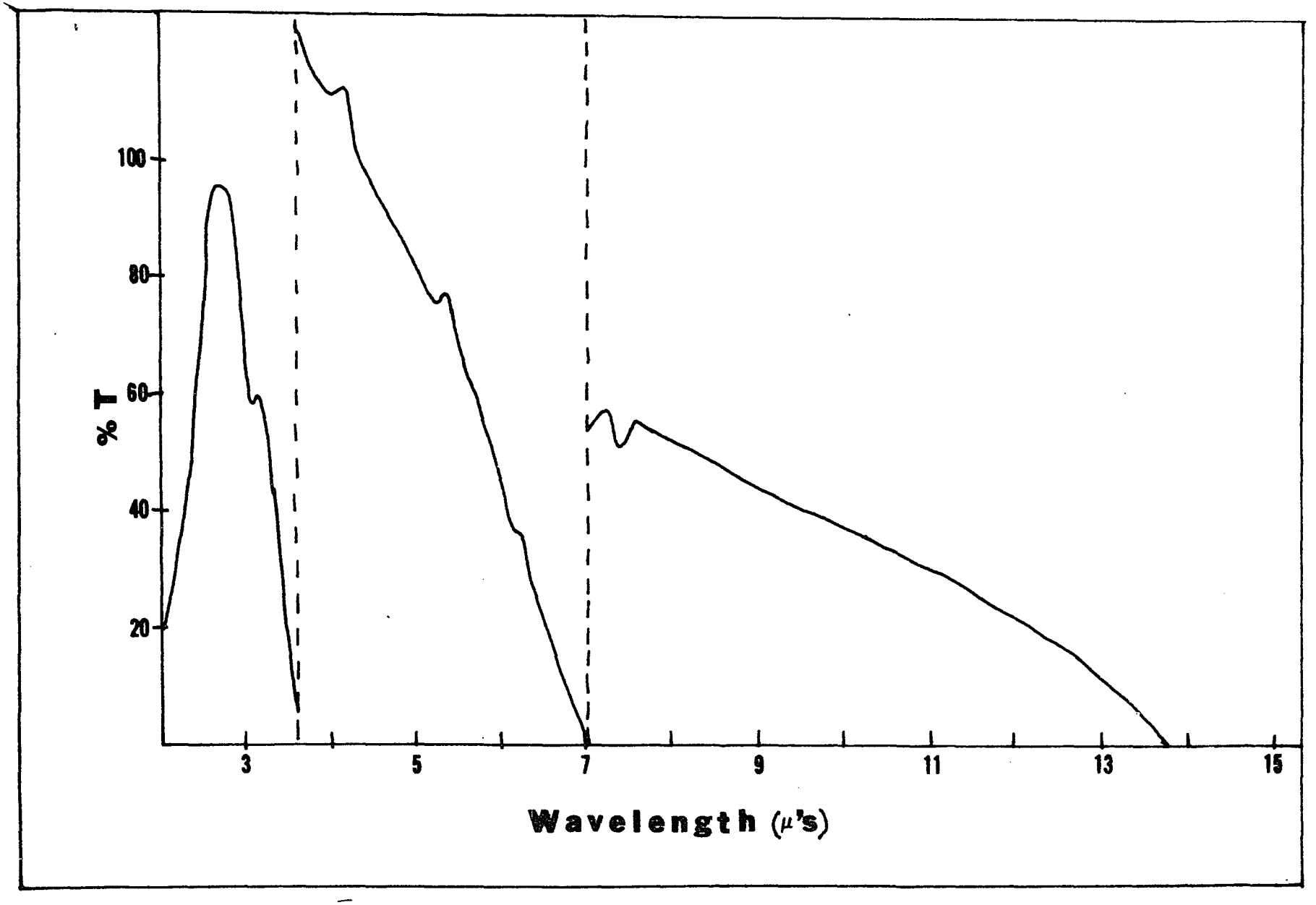
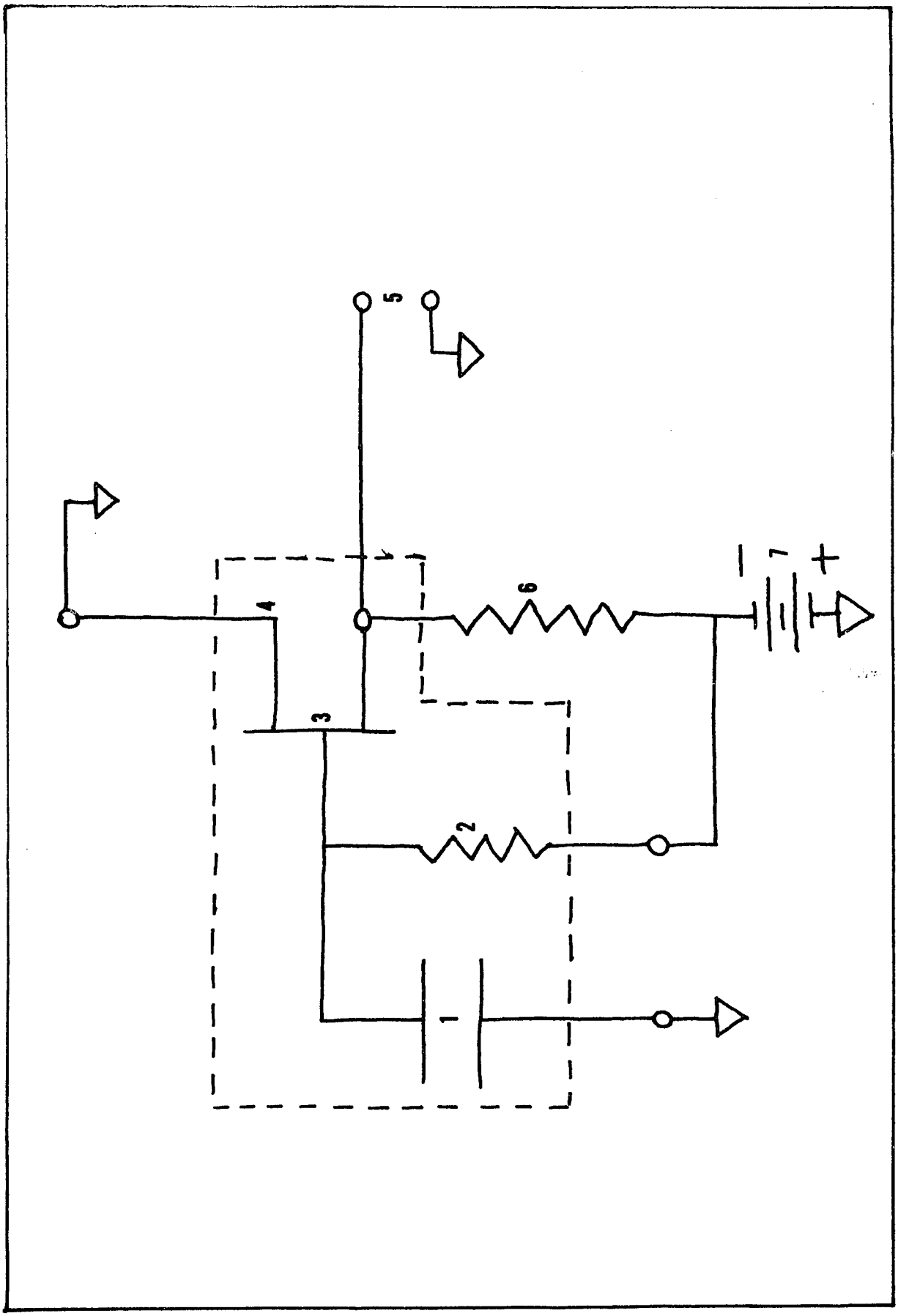

100
80
60
40
20
% T
3
5
7
9
11
13
15
Wavelength (μ's)

Figure 27

ORIGINAL BARNES DETECTOR CIRCUIT

1. Pyroelectric Element
2. Load Resistor (10^{12} Ohms)
3. Gate
4. Drain
5. Output
6. 55 k Ohm Resistor
7. 24 Volt Battery


5
4
6
3
2
1
-
+

The factory-tested responsivity (R) was 884 volts per watt, and the detectivity (D*) was 6.13 times 10^8. A twenty-four volt battery box and 68K resistor were installed. When tested, the detector would not detect a match held in front of it. It was sent back to Barnes; and when returned, it was tested again. (The flux from a 800 degree Centigrade blackbody was first measured with the power meter, and then the detector.) The responsivity was about two orders of magnitude lower than the specifications. This was due to the fact that Barnes had included their preamplifier (gain = 105) in their calculations.

It was found that the responsivity seemed to be decreasing with time. Pyroelectric detectors use thin dielectric slabs on whose faces an electrostatic charge appears when their temperature is changed. The dielectric slab must be polarized for the detector to work properly. If the detector is subjected to various forms of stress, the residual polarization is lost. It must then be repolarized. A circuit can be built which will prevent the loss of polarization. Such a circuit, shown in Figure 28, was built for the Barnes detector and has been used in this study.

The detectivity is defined by the following:

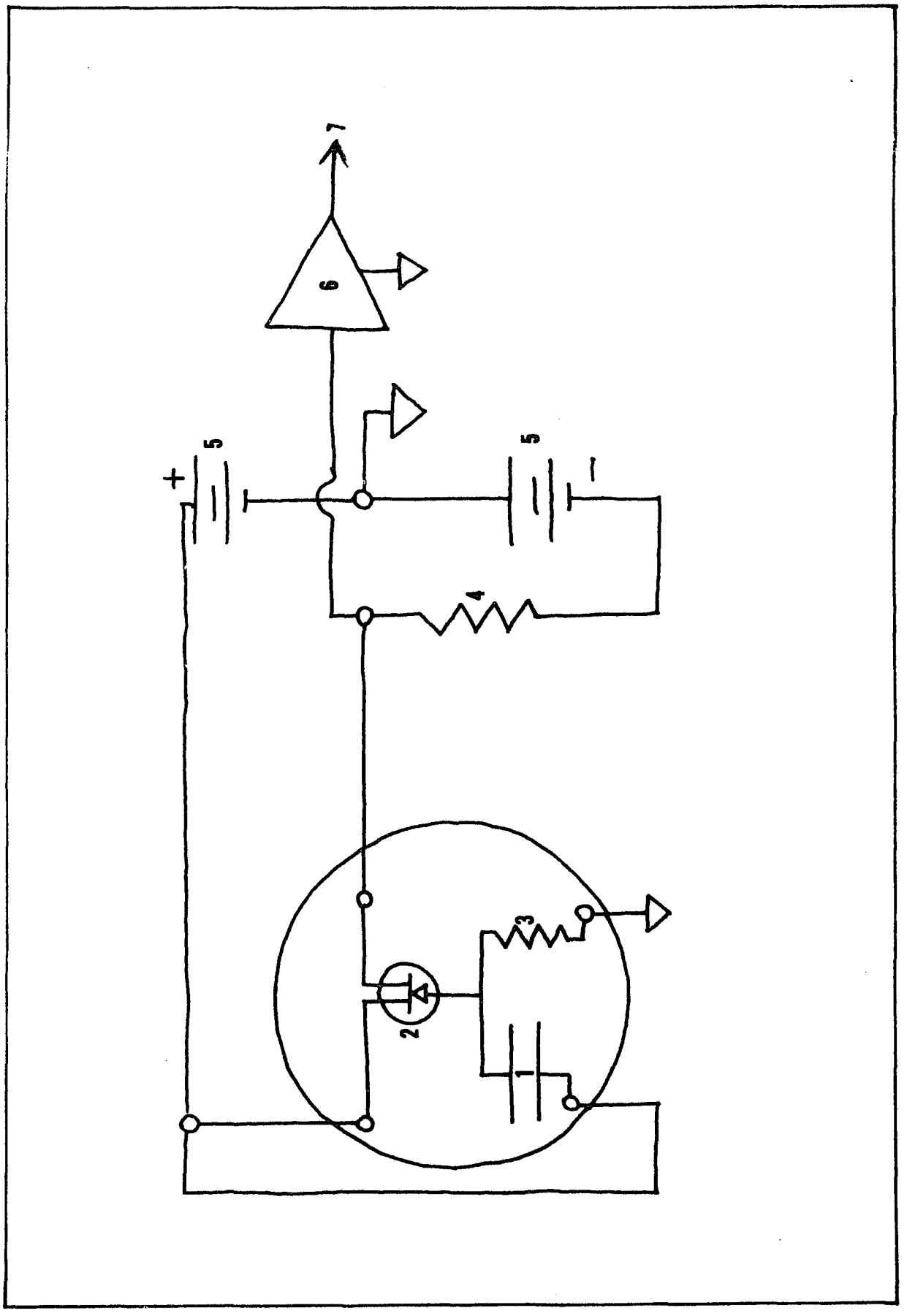
$$D^* = (S/P_o N)\ (\Delta f/A)^{\frac{1}{2}} \qquad 33$$

where S is the signal (in volts) produced by the detector when a flux of P_o (in watts) falls upon it. N is the noise level

Figure 28

SECOND BARNES DETECTOR CIRCUIT

1. Pyroelectric Element
2. MOSFET
3. Load Resistor (10^{12} Ohms)
4. 22 k Resistor
5. 12 Volt Battery
6. Preamplifier
7. Output


7
6
5
+
1
5
1
4
3
2

(in volts), and Δf and A are the band width of the system (in Hz) and the area of the detector (in square centimeters), respectively.

When the quality factor of the amplifier (Q) was set to 100, the band width was 10.5 Hz. The area was 0.04 square centimeters, and the noise level was determined to be about 80 nanovolts. This Q-setting was used throughout this study.

It can be seen that S/P_o is just the responsivity (R) which has been calculated already and determined to be four volts per watt. Therefore,

$$D^* = (R/N)\ (\Delta f/A)^{\frac{1}{2}}$$

$$D^* = (4/8.0 \times 10^{-8})\ (10.5/0.04)^{\frac{1}{2}}$$

$$D^* = 8.1 \times 10^{8}$$

which is almost exactly the published specifications.

It was observed that when the amplifier was phase- and frequency-locked onto the chopper, there was a negative signal of about one microvolt. When the system was first turned on there was no such signal, but it built up with time and equilibrated after a matter of minutes. This signal was observed to be positive when the amplifier was just frequency-locked. When an infrared opaque object was placed in front of the chopper, the signal remained; but when the object was placed between the chopper and monochromator, the signal ceased. The metal chopper blade felt hot to the touch. When a chopper blade was made from a non-heat-conducting material (Bakelite), the problem signal ceased.

Changes in the chopping frequency seemed to make little difference in the sensitivity of the system. The sensitivity dropped slowly with the increasing frequency, but the noise level dropped also. The optimum frequency was 26 Hz and most of the experiment was done at this frequency.

Since the a.c. power to the plasma tube was at a frequency of 120 Hz, this frequency was tried and the amplifier was locked on it. This was done by hooking a small transformer (output one-quarter volt) parallel to the 15,000 volt transformers and locking onto the one-quarter volt signal. A scatter signal was obtained from a piece of IRTRAN II at this frequency with no chopper, but the intensity was much lower than that obtained with the chopper. This indicated that the laser signal was essentially continuous with a small amount of 120 Hz a.c. ripple.

All noise in the system could be traced to the detector, even when it and all other detector components were shielded and grounded scrupulously. The noise seemed to be least when new batteries were installed in the detector power supply, and also in the middle of the day. The noise was highest when the batteries were getting old, and near the end of the day. For the former, the author has no explanation; but the latter was believed to be due to the fact that many electrical appliances were being turned off in the building, causing large variations in the line current.

OZONE GENERATOR OPERATING PARAMETERS

When the project was first begun, a General Electric OZ-4 lamp was used to generate ozone. One of these lamps was placed in a glass vessel of about three-liter capacity. The vessel was sealed with rubber stoppers coated with parafin wax. Oxygen was passed through the vessel and ozone was formed. At this time, the formation of ozone was detected by smell.

The OZ-4 lamps were small mercury lamps which were enclosed in quartz. They cannot be hooked directly to line current, but must be placed in series with a ballast. The ballast used in this case was a 100-watt light bulb.

It has been seen that the photochemical method of ozone production was very inefficient, and this type of apparatus gave yields in the part per million concentration range. It has been seen that photochemical production of ozone occurred with light below the 2000 to 2100 angstrom wavelengths.[34] Quartz transparency drops off rapidly below 1850 angstroms, so the active radiation must occur between these two limits.

The Perkin-Elmer laser beam was passed through a cell filled with the ozone-oxygen mixture produced by the OZ-4 lamp apparatus. No detectable ozone absorption or emission occurred. The tunable laser was tried through all of its wavelengths

with the same results. Two OZ-4 lamps were placed in the aforementioned vessel. When the laser experiments were attempted, they failed also. The oxygen flow rate was adjusted throughout the range of the rotameter that was used.

Next, the modified silent-discharge apparatus, which has been described in the Equipment section, was built. Three sizes of West condensor were tried. The concentration of ozone was inversely dependent upon the size of the condensor used; therefore, the smallest one was settled on for this study.

The silent-discharge apparatus is usually made from a material such as stainless steel and is water-jacketed. Ozone will thermally decompose and the walls of the apparatus are heated by the passage of the electric current.

With time, the concentration stability of the apparatus was checked by the absorption of 9.6 micron radiation by ozone. The results are shown in Figure 29.

The absorption spectrum of ozone in the infrared region is shown in Figure 30.[35] It is easily seen that the absorption band between nine and ten microns was the strongest.

The assignment of the fundamental vibrations of ozone were first made correctly by Wilson and Badger.[36] The assignments were as follows:

$$V_1 = 1110\ cm^{-1} \quad (9.0\ microns),$$

$$V_2 = 705\ cm^{-1} \quad (14.2\ microns), \text{ and}$$

$$V_3 = 1043\ cm^{-1} \quad (9.6\ microns).$$

Figure 29

TIME STABILITY OF OZONE GENERATOR

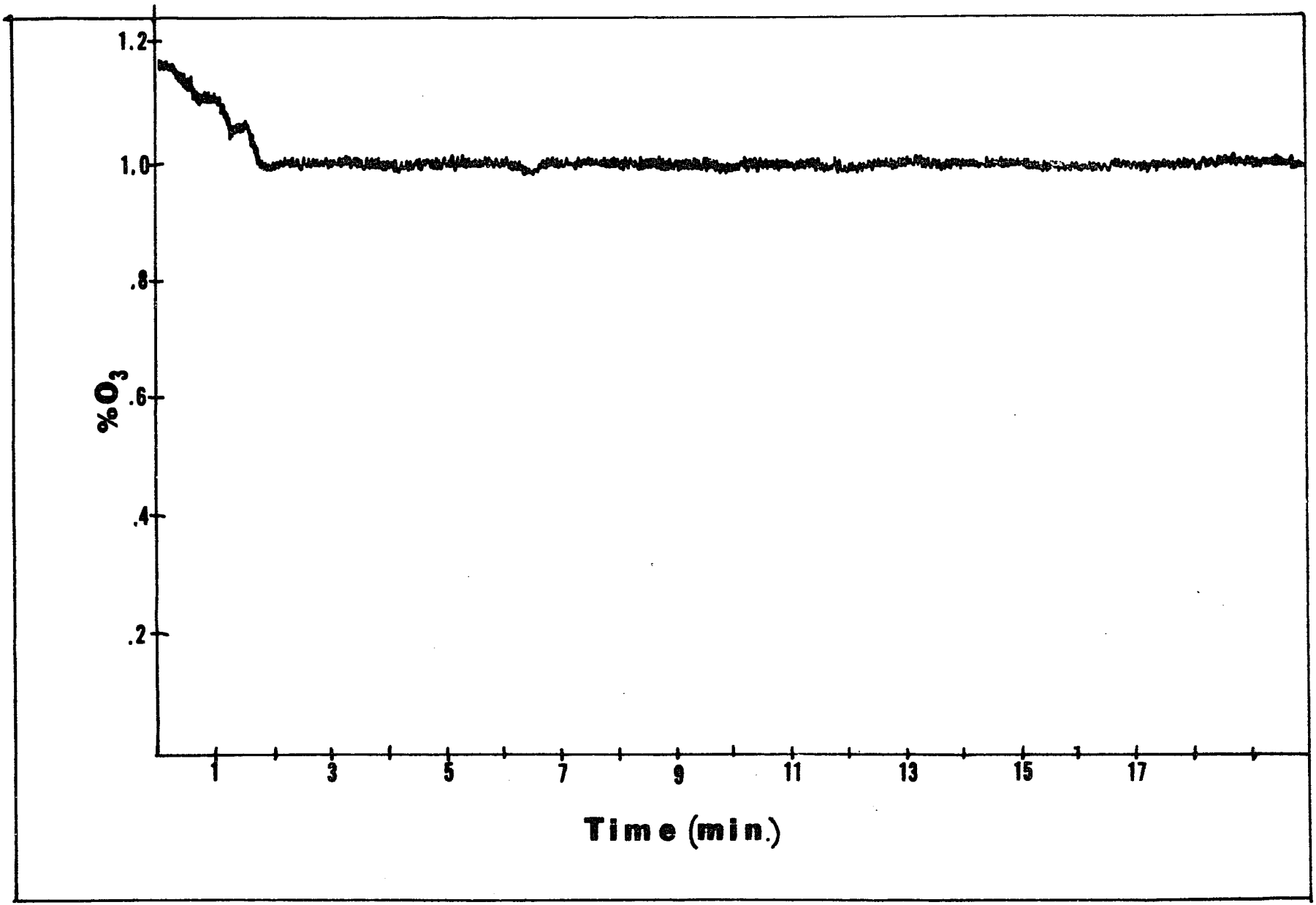
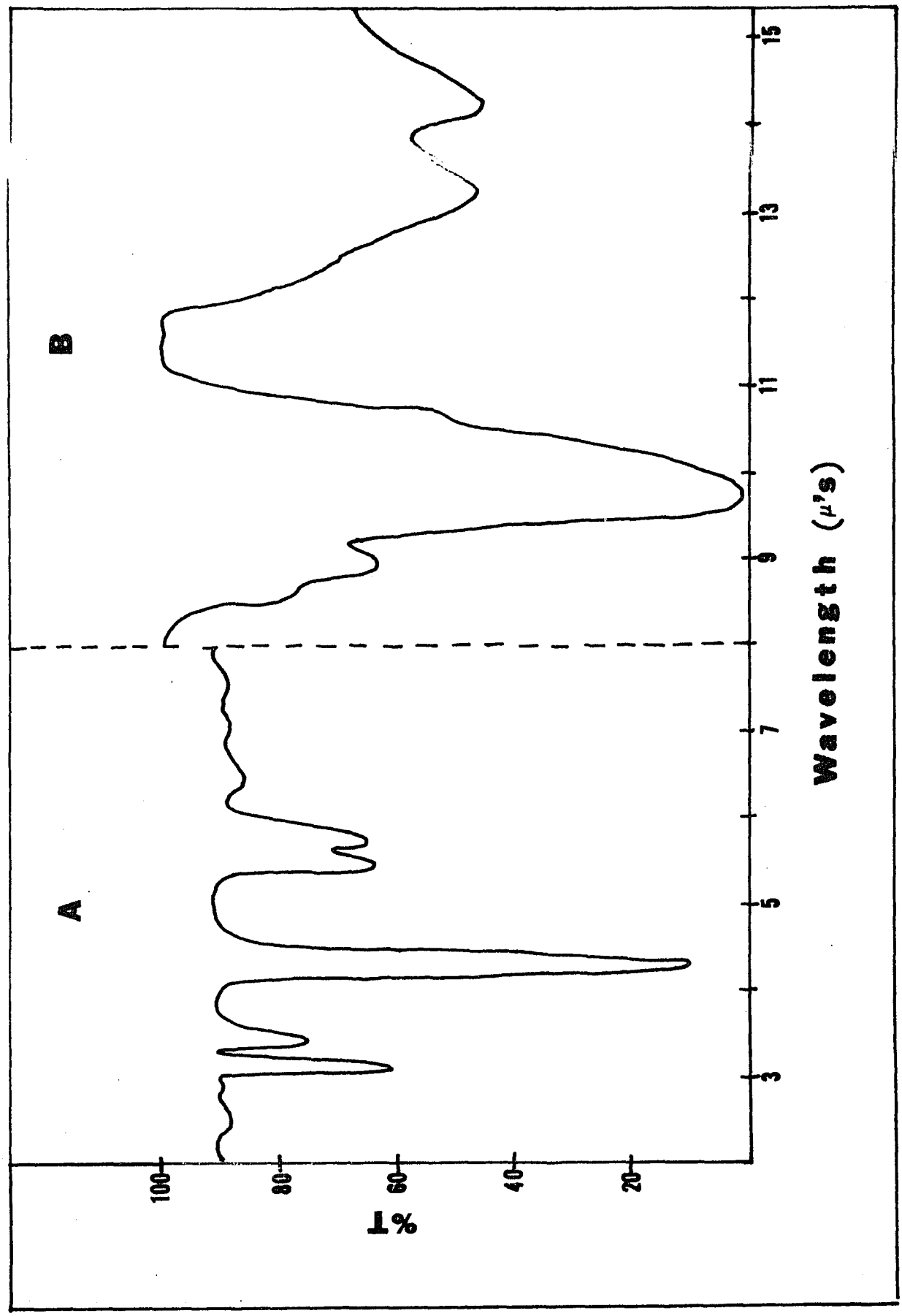

1.2
1.0
.8
.6
.4
.2
%O3
1
3
5
7
9
11
13
15
17
Time (min.)

Figure 30

ABSORPTION SPECTRUM OF OZONE

A. 230 Millimeter Partial Pressure
B. 160 Millimeter Partial Pressure

(After Herzberg)


A
B
%T
100
80
60
40
20
3
5
7
9
11
13
15
Wavelength (μ's)

The extinction coefficients of these bands were 0.05, 0.08, and 6.0, respectively. These assignments were confirmed much later by Raman studies.[37] The Raman studies had to wait until the ozone could be separated from the oxygen effectively.

By knowing the extinction coefficient, path length, and absorbance, the efficiency of the ozone-generating apparatus can be checked. The concentration of ozone generated was varied by changing the flow rate of oxygen through the silent-discharge apparatus. When the oxygen flow rate was changed from 150 to 1300 milliliters per minute, the ozone concentration changed from 1.2 per cent to 0.2 per cent.

The relationship between the ozone concentration and oxygen flow rate was determined in the following way. First, the concentration was calculated using Beer's Law ($-\log I/Io = abc$). By determining absorbance ($-\log I/Io$) and inserting the values for the extinction coefficient (a) and the path length (b), the concentration (c) can be calculated.

A second plot was made using a second cell with a length of approximately (2b).

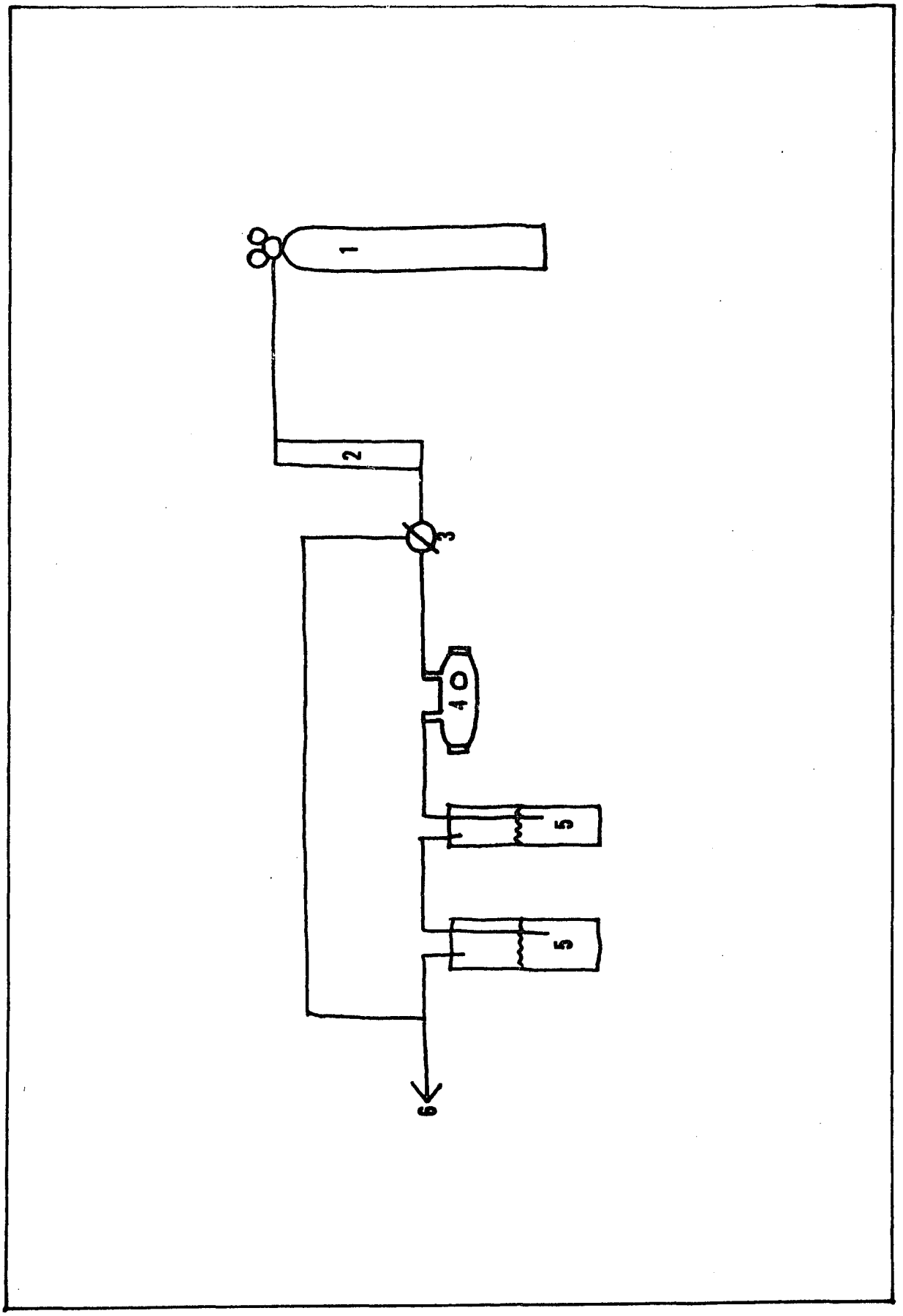
Finally, a standard method[38] for ozone (in the percentage concentration range) was employed for three of the flow rates; and these values were checked against the values which were obtained by the Beer's Law method.

The method employed a potassium-iodide solution through which the ozone mixture was bubbled, (Figure 31) and then titrated with thiosulfate standard.

Figure 31

OZONE SCRUBBER SYSTEM

1. Oxygen Tank
2. "Silent-Discharge Generator
3. Three-Way Stopcock
4. Fluorescence Cell
5. Scrubber (Potassium-Iodide Solution)
6. Vent


1
2
3
4
5
5
6

Saturated potassium-iodide solutions were used and the ozone mixture was allowed to flow for two minutes through the scrubbers before being switched back through the small cell.

The contents of the second scrubber took very little more thiosulfate than the blank, attesting to the efficiency of the first scrubber.

The results of these experiments are summarized in Table 2.

Table 2

O_2 Flow Rate (ml/min)	20 cm ($\%O_3$) Beer's Law	44.5 cm ($\%O_3$) Beer's Law	($\%O_3$) KI Method
150 [a]	1.1	1.2	1.0 [b]
250	0.72	1.0	0.8 [b]
450	0.52	0.70	0.7 [b]
700	0.34	0.50	---
900	0.28	0.45	---
1060	0.24	0.35	---
1300	0.20	0.28	---

[a]These increase by two units on the rotameter used from 2-14.

[b]Each is the average of three runs.

OZONE FLUORESCENCE

It was found that when the beam from the Perkin-Elmer laser was passed through a cell filled with a one per cent ozone-oxygen mixture, no detectable absorption occurred. Also, no detectable infrared fluorescence was observed arising from the ozone. Therefore, further studies on ozone were carried out using only the tunable carbon dioxide laser.

The first thing which was done was to find which one of the four lasing bands of the tunable carbon dioxide laser would ozone absorb. This was a coarse tuning experiment--a fine tuning experiment will be described in a later section.

It was found that the 9.6 micron band (the P Branch of the $00^{\circ}1$--$02^{\circ}0$ transition) was the only one which was absorbed. Therefore, unless otherwise stated, all experiments were done with the lasing wavelength around 9.6 microns.

The fluorescence from ozone was first observed without the monochromator system. The detector was simply directed at the fluorescence window of the small cell. The chopper was placed between the cell and the detector. The signal level was taken with the laser on, but no ozone (only oxygen) was flowing through the cell. Then, the ozone generator was turned on and ozone flowed through the cell. The signal with ozone in the cell was recorded. When the two signals were

subtracted, the difference was the net signal from ozone. Three pieces of information were obtained from this experiment. The first was that there was ample signal coming from ozone to use the monochromator, unless the signal was just broadband emission spread throughout the entire middle infrared region.

The second discovery was that measures must be taken to limit the field of view of the detector. With the chopper very close to it, the detector could "see" almost 180 degrees around itself. It would detect any warm bodies that came into its field of view, people included.

The third fact discovered in this experiment was that the silent-discharge ozone generator was too electrically noisy to be used as it was. The generator was placed in the center of a cage measuring about two feet cubed. The bottom of the cage was an aluminum scaffolding rack (two feet square in measurement). The skeleton of the cage was aluminum scaffolding covered on three sides with aluminum foil, and on top and one side with fine copper screen. The cage and transformer case were grounded to a water pipe nearby. The line circuit to the detector system was isolated from the line circuit to the transformers in the laser power supply and the transformer to the ozone generator. Aluminum foil was placed so as to cover all the detector mount except the detector window and this was grounded. After all this was done, the

ozone generator could be switched on without affecting the detector noise-level at all.

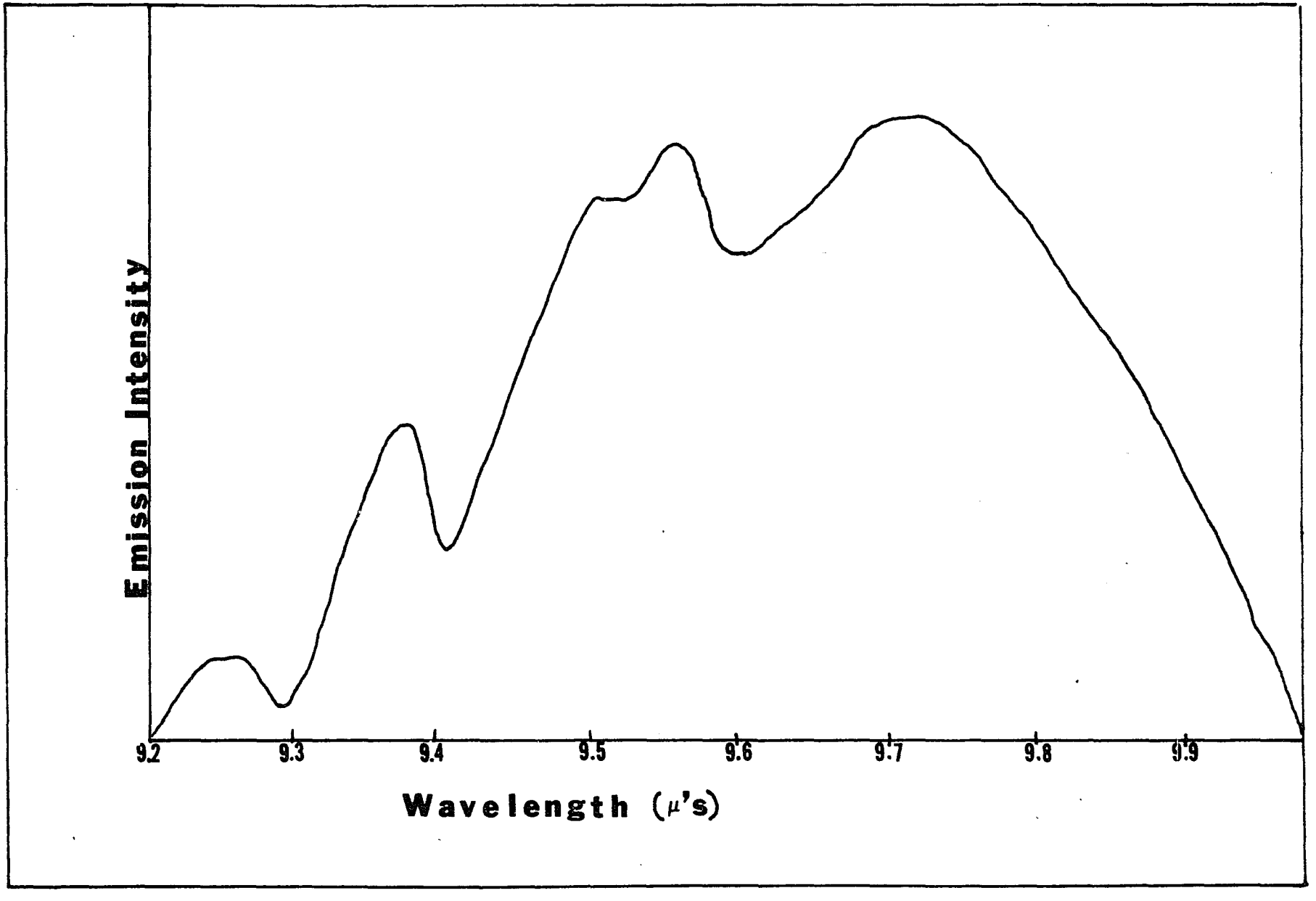
The next experiment done was to place the filter wheel in front of the detector and try to isolate the emission signal to one of the regions covered by the filters. As shown in Figure 25, the filter domains overlapped somewhat. With Filter Two, a 1.5 microvolt signal was obtained. With Filter Three, a 150 microvolt signal was obtained. But with Filter Four, a 500 microvolt signal was obtained. This means that the emission observed came between seven and fourteen microns but was closer to the shorter wavelength end.

Next, the detector was installed on the monochromator and the entire region from 1.7 microns to 14 microns was scanned. The ozone fluorescence which was observed is shown in Figure 32.

It was seen that the fluorescence band between nine and ten microns in Figure 32 is very similar to the V_3 absorption band in Figure 30. It was further noted that there was no emission detectable from the V_1 band, even when irradiated with the 9.2 micron line of the tunable laser. There was no fluorescence observed from the V_2 band, although it was near the limits of the windows used. None of the combination bands were observed to fluoresce detectably either.

Figure 32

OZONE INFRARED FLUORESCENCE SPECTRUM


Emission Intensity
9.2
9.3
9.4
9.5
9.6
9.7
9.8
9.9
Wavelength (μ's)

EFFECTS OF FINE TUNING OF THE LASER WAVELENGTH

There are about seventy discrete wavelengths for which lasing action occurs in a carbon dioxide laser. Studies were made at each wavelength separately. Some of the lines on the edges of the gain curves gave such low power that they were essentially useless. This left about fifty-five useful lines.

The power transmitted through the cell seemed to be the same for oxygen as that for the other non-absorbing gases which were used. Therefore, the absorption of ozone was determined as the difference in the absorption of (a) oxygen, and (b) oxygen plus ozone.

The transmitted power through the oxygen-filled cell for each wavelength gave the relative power of that wavelength. The results of this experiment are shown in Figure 33.

The relative power of each line passing through the ozone-oxygen filled cell, when compared to Figure 33, gave the absorption spectrum seen in Figure 34.

Simultaneously, from the same cell, the emission at 9.6 microns was monitored in a direction perpendicular to the laser beam. The dependence of the 9.6 micron emission on the lasing wavelength is shown in Figure 35. Its dependence upon ozone concentration is shown in Figure 36.

Figure 33

TRANSMITTED POWER OF CARBON DIOXIDE LASING LINES

(BETWEEN 9.46 AND 9.64 MICRONS)

THROUGH OXYGEN FILLED FLUORESCENCE CELL

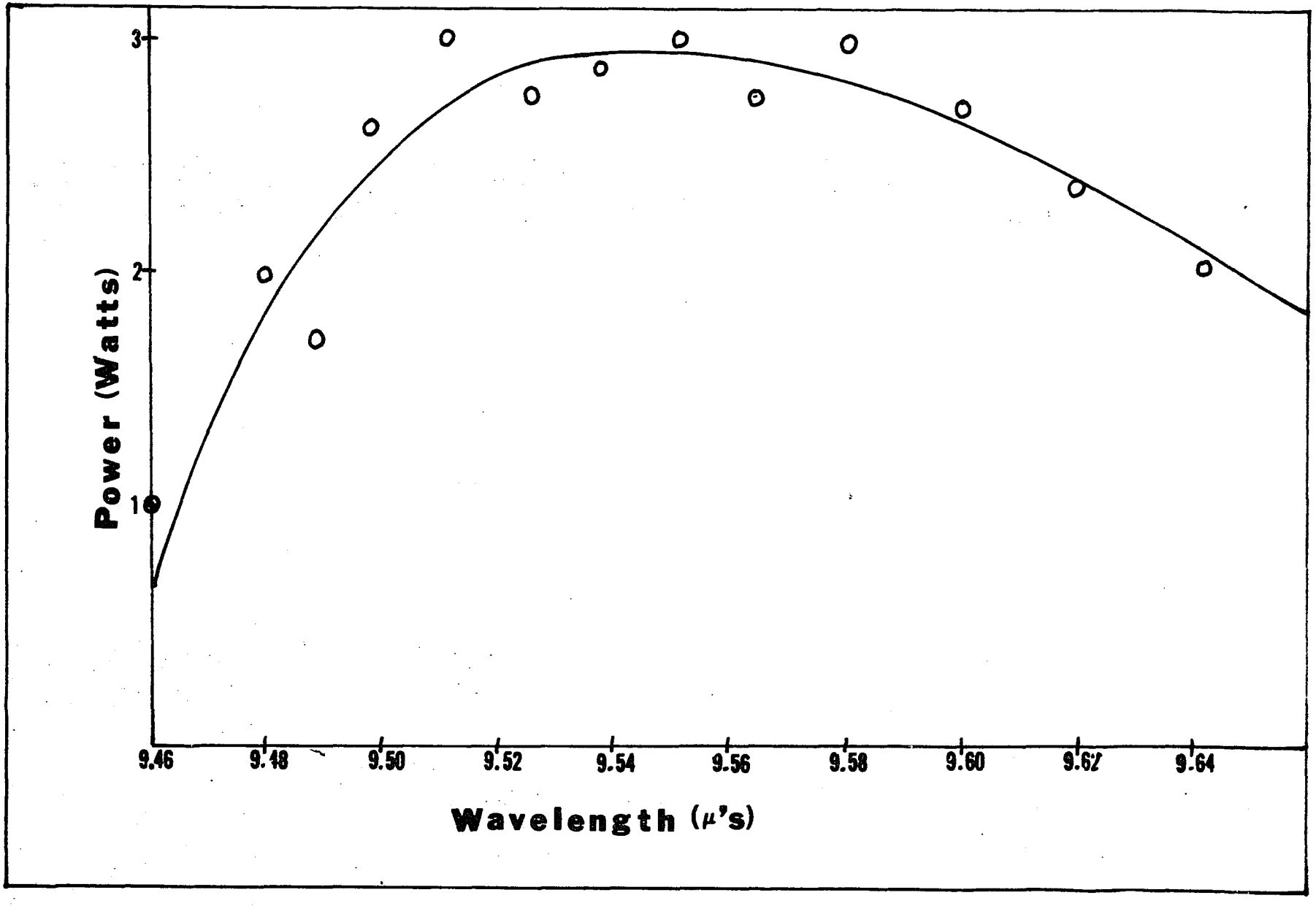

Power (Watts)
3
2
1
9.46
9.48
9.50
9.52
9.54
9.56
9.58
9.60
9.62
9.64
Wavelength (μ's)

Figure 34

ABSORPTION SPECTRUM OF OZONE

(BETWEEN 9.46 AND 9.64 MICRONS)

FROM THE ABSORPTION OF CARBON DIOXIDE LASING LINES

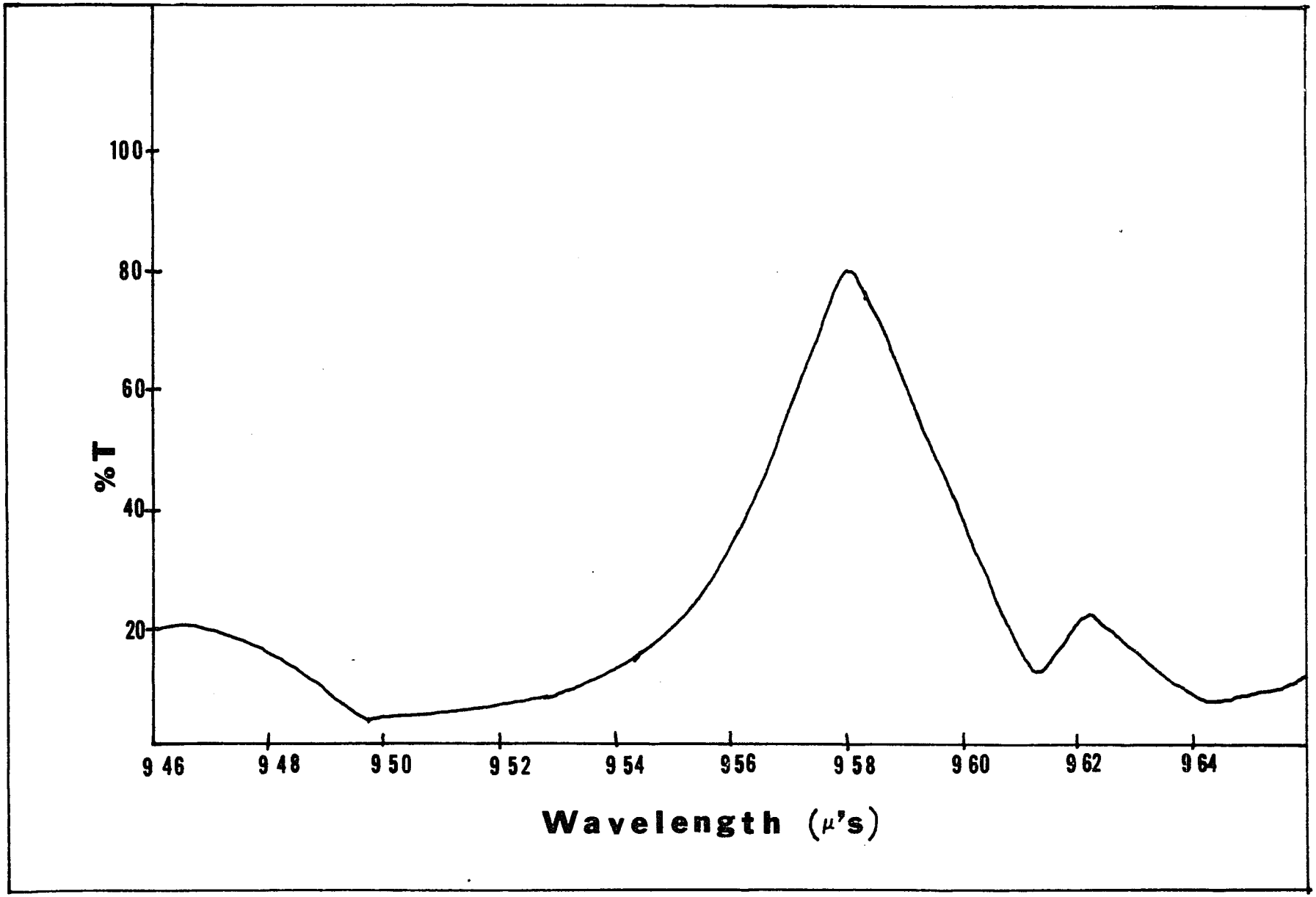

100
80
60
40
20
%T
9 46
9 48
9 50
9 52
9 54
9 56
9 58
9 60
9 62
9 64
Wavelength (μ's)

Figure 35

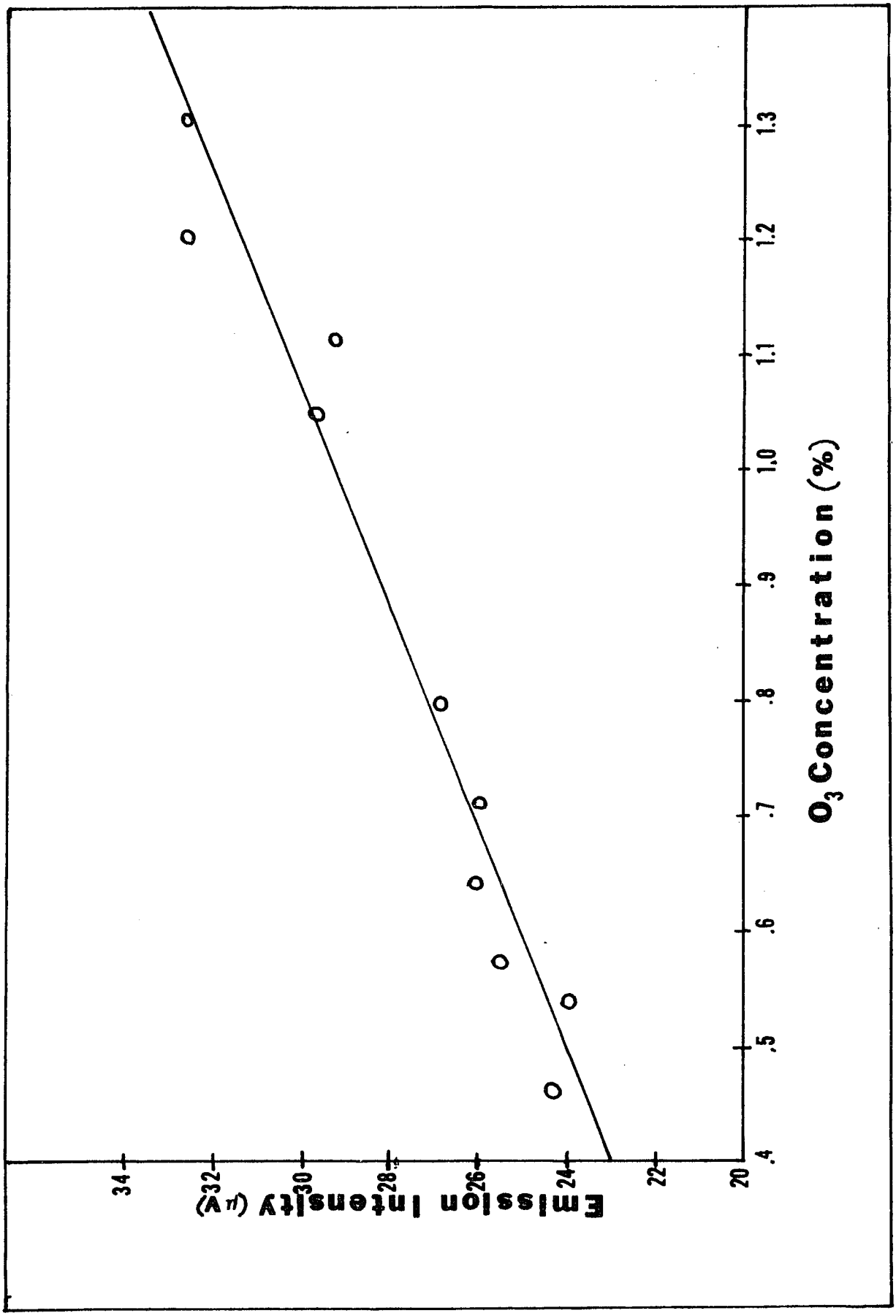
DEPENDENCE OF THE FLUORESCENCE INTENSITY AT 9.6 MICRONS ON THE WAVELENGTH OF THE EXCITING LASER LINE

Emission Intensity
20
40
60
80
100
120
Wavelength, μ's
9.46
9.48
9.50
9.52
9.54
9.56
9.58
9.60
9.62
9.64

Figure 36

DEPENDENCE OF FLUORESCENCE INTENSITY

UPON OZONE CONCENTRATION


Emission Intensity (μV)
34
32
30
28
26
24
22
20
.4
.5
.6
.7
.8
.9
1.0
1.1
1.2
1.3
O_3 Concentration (%)

The micrometer adjustment on the horizontal drive of the grating mount was standardized using the monochromator. This was done before placement of the cell by scattering radiation off a piece of rough transite. For this study, the slits of the monochromator were set at about two microns. This allowed very precise determination of the lasing wavelengths.

The lasing line width was observed to decrease with decreasing slit width until the signal was undetectable. (The resolution of the system with the 75 groove per millimeter grating was about twenty angstroms with ten-micron slits.) The slits were set at 200 microns for the study of 9.6 micron emission versus lasing wavelength. This means that, although the monochromator was set at 9.6 microns, a band of 2000 angstroms (9.5 to 9.7 microns) was being measured.

It can be seen that minor changes in laser wavelength (e.g., 9.56 to 9.58 microns) resulted in major changes in the degree of absorption by ozone.

Simultaneously, the fluorescence intensity varied considerably in a direct relationship to the degree of absorption observed. This occurred even though there was no similar change in the power output of the laser at these wavelengths.

OZONE FLUORESCENCE LIFETIMES AND LASER BEAM CHOPPING

It was seen that there was no cell heating accompanying the injection of ozone into the cell. Furthermore, blockage of the beam produced an immediate drop in the fluorescence signal. These factors led to the fact that ozone is directly excited by the laser radiation at 9.6 microns.

When attempts were made to chop the laser beam, a large "scatter" signal seemed to be produced. No realignment of the cell seemed to get rid of it. The signal seemed to remain the same whether ozone was introduced into the cell or not.

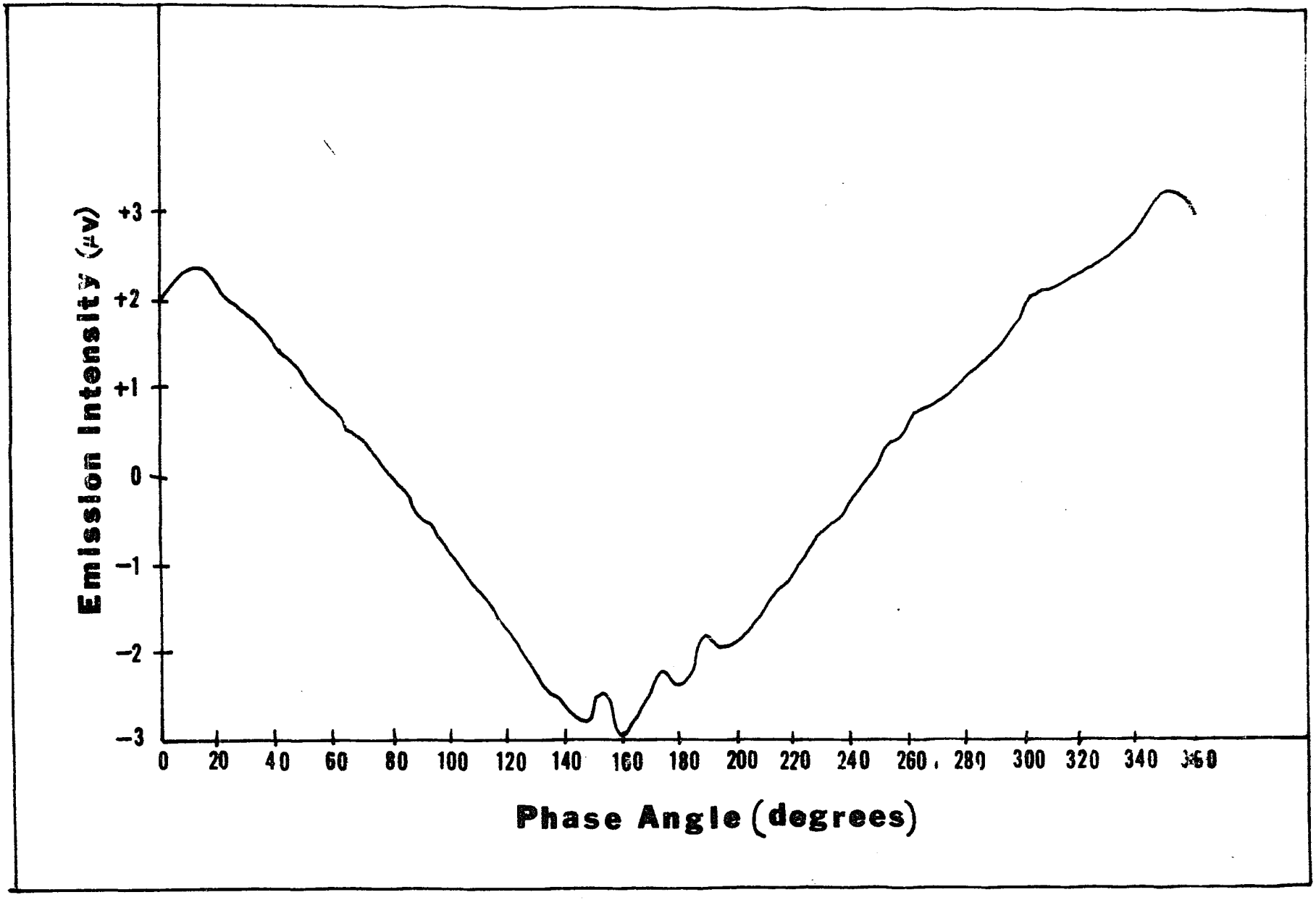
If this was a simple scatter signal, and if the lifetime (radiative) of the ozone was of the right order of magnitude, proper phasing would remove the scatter signal and detect only the fluorescence. To this end, the following experiments were done.

First, the cell was filled with oxygen and the phase of the amplifier was changed in five degree increments from 0 to 360 degrees. This means that one cycle of the chopper (1/13 Hz or 78 milliseconds) was broken up into seventy-two segments (360 degrees/5 degrees) and the signal occurring in each segment was measured. This experiment generated Figure 37.

Figure 37

DEPENDENCE OF OXYGEN-FILLED CELL

SCATTERING INTENSITY UPON PHASE ANGLE AT 13 Hz


Emission Intensity (μv)
+3
+2
+1
0
−1
−2
−3
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
Phase Angle (degrees)

Then, the same type of experiment was performed with a one per cent ozone-in-oxygen mixture. The results of this are shown in Figure 38.

Subtracting Figure 37 from Figure 38 should give the intensity of the ozone signal versus phasing (or time). This is shown in Figure 39.

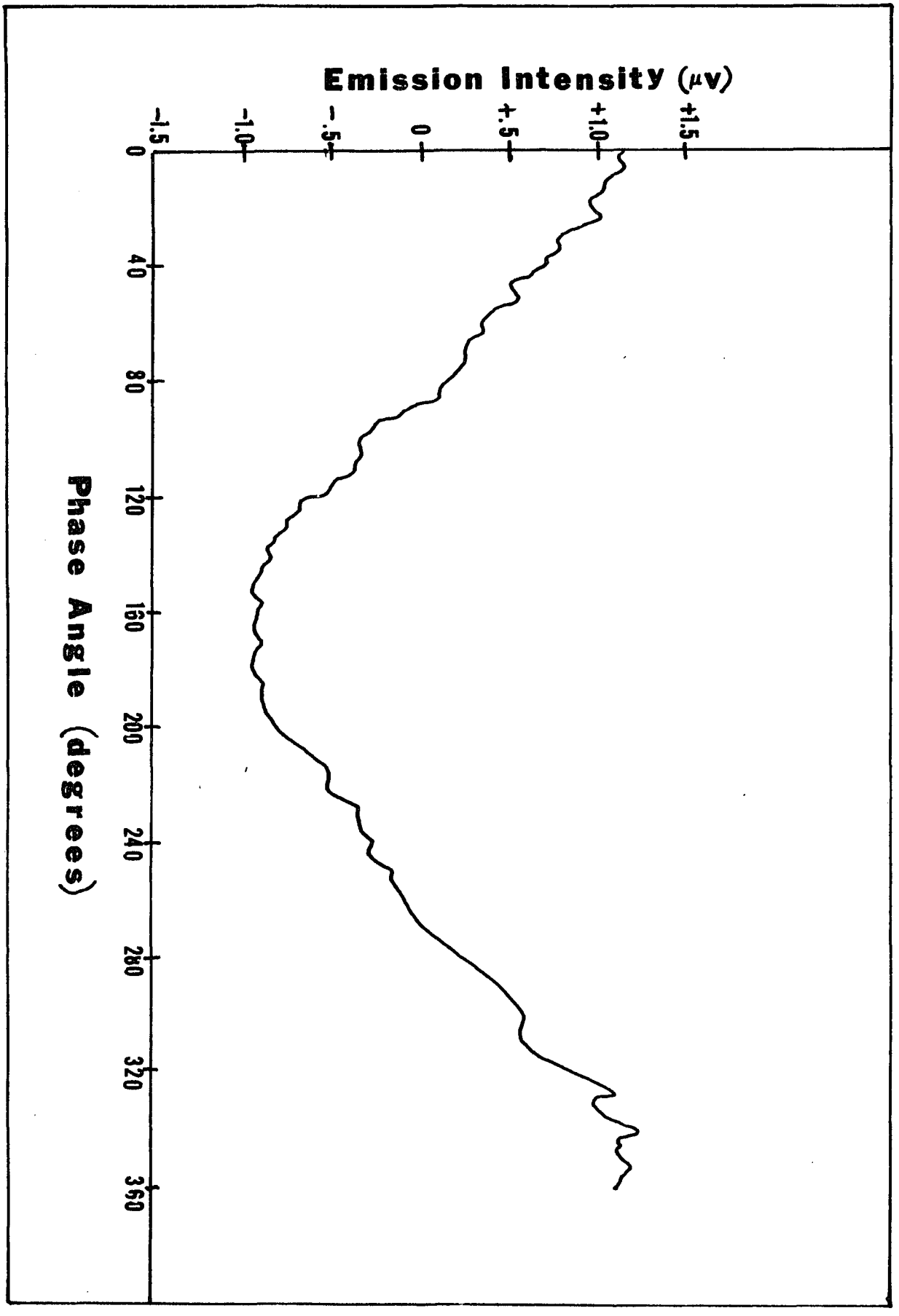
The ozone seemed to absorb the scatter signal somewhat and a multiplicative or weighting factor of about two was introduced in the calculation of Figure 39 to account for this.

It is difficult to tell whether or not these data are any good. Figure 39 is the average of a number of runs of this experiment. The chopping of the laser beam was discontinued; and in all subsequent experiments, the fluorescence was chopped.

The use of a box car integrator and a storage type oscilloscope, or interfacing the experiment with a minicomputor would probably generate valid data.

Figure 38

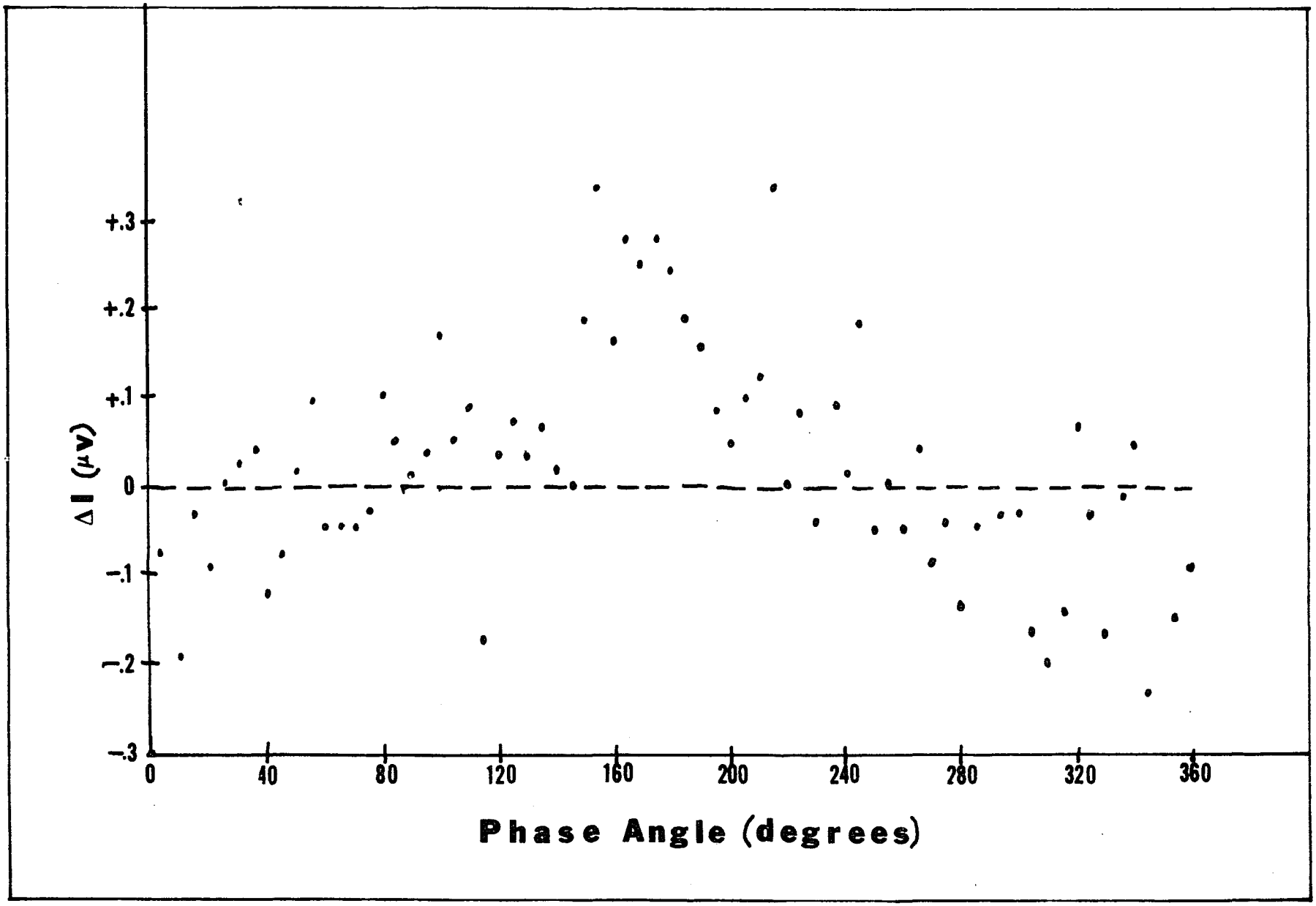
DEPENDENCE OF OZONE-OXYGEN FILLED CELL SCATTERING INTENSITY UPON PHASE ANGLE


Emission Intensity (μv)
-1.5
-1.0
-.5
0
+.5
+1.0
+1.5
0
40
80
120
160
200
240
280
320
360
Phase Angle (degrees)

CCT

Figure 39

RESULTS OF SUBTRACTION OF
OXYGEN SCATTERING VERSUS PHASE ANGLE AND
OZONE-OXYGEN SCATTERING VERSUS PHASE ANGLE


+.3
+.2
+.1
0
-.1
-.2
-.3
ΔI (μV)
0
40
80
120
160
200
240
280
320
360
Phase Angle (degrees)

EFFICIENCY OF CONVERTING LASER RADIATION TO FLUORESCENCE

To get some idea of the efficiency of the radiation-absorption-emission process being studied, the following calculations were made.

It was assumed that all radiation which passed through the slits was detected. It was further assumed that reflection of the fluorescence from the walls of the cell into the slits was negligible. Also, the absorption and fluorescence was assumed to be uniform along the length of the beam inside the cell. (This was convenient, but definitely not true.)

The slits, when wide open, were two millimeters wide and two centimeters high, thus constituting an area of 0.4 square centimeters. The slits were ten centimeters from the center of the beam, and the cell was twenty centimeters long.

From the above dimensions, the area of an imaginary cylinder of radiation was calculated:

$$A_c = 2\pi rh + 2(\tfrac{1}{2})4\pi r^2$$

$$A_c = 2.50 \times 10^4 \text{ square centimeters.}$$

This area is proportional to the total emission from the molecules contained within the laser beam. This is then ratioed with the area of the slits:

$$A_s/A_c = 0.4/2.50 \times 10^4$$

$$A_s/A_c = 1.5 \times 10^{-5}$$

This factor should give some indication of the fraction of the fluorescence which was entering the slits.

The responsivity of the T.G.S. detector was measured and found to be four volts per watt. The signal obtained during this experiment was about two microvolts. It is then seen from $R = S/P_o$

that $P_o = S/R$,

therefore $P_o = (2 \times 10^{-6} \text{ volts}) / (4 \text{ volts/watt})$

$P_o = 0.5 \times 10^{-6}$ watts.

This means that one-half microwatt was falling on the detector.

There was an IRTRAN II window on the cell and one on the entrance slit of the monochromator. They each attenuated the radiation (at about 9.6 microns) passing through them by a factor of twenty-five per cent. The Number Four Filter in the order-sorter was seen in Figure 25 to be about eighty-five per cent transmissive at 9.6 microns. The window of the detector is KRS-5 and transmitted about seventy per cent.

By combining these transmisivities,

$$(0.75)\ (0.75)\ (0.85)\ (0.70) =$$

one arrives at a factor of 0.34 for the total attenuation by windows and filters. The percentage of the total fluorescence contained in the band seen by the detector, with the slits wide open and the monochromator set at 9.6 microns, was about twenty per cent.

This means that the ratio of the area of the fluorescence band between 9.5 and 9.7 microns to the area of the entire fluorescence band was 0.20.

The energy absorbed by the one per cent ozone-in-oxygen mixture was about four watts (four watts transmitted from an eight-watt beam).

From the above factors it was seen that

$$\frac{0.5 \times 10^{-6} \text{ watt}}{(1.5 \times 10^{-5})\ (0.34)\ (0.20)}$$

or

$$\frac{0.5 \times 10^{-6} \text{ watt}}{1 \times 10^{-6}}$$

or about one-half watt of the absorbed radiation is re-emitted as fluorescence.

This means that the efficiency of conversion was therefore

$$0.5/4 = 0.125$$

or about 12.5 per cent.

The above was only an "order-of-magnitude" type calculation, but it does indicate that a rather large percentage of the laser radiation was converted to vibrational energy.

ANALYTICAL SENSITIVITY

The analytical sensitivity of the system was determined from the following calculations and assumptions.

It was assumed that the detector "saw" radiation only from a cylinder two centimeters in diameter (the diameter of the beam) and two millimeters in height (the width of the slits). This means that the effective volume monitored which was generating radiation falling on the detector was

$$2\pi rh = \pi(2)\ (0.2),$$

about 0.6 milliliter. At one per cent concentration, this corresponds to about

$$\frac{\text{(volume) (concentration)}}{\text{(molar volume)}} = \frac{(0.6)\ (0.01)}{(2.24 \times 10^{4})}$$

2.8×10^{-7} mole of ozone, or

$$(2.8 \times 10^{-7})\ (48) = 13.4 \times 10^{-7} \text{ grams}$$

about 1.34 micrograms.

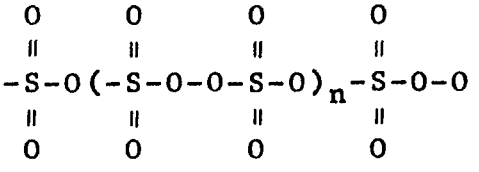
Since the signal detected for this concentration was about two microvolts, and since about 100 nanovolts can be detected above noise (S/N = 2), it would be expected that about seventy nanograms of ozone would give detectable emission.

INTERFERENCES

An attempt was made to study the effects of interferents on the fluorescence intensity of ozone. Unfortunately, the ozone was in such high concentration that it reacted with all but the most inert gases. With these gases (nitrogen, carbon dioxide, and helium) there seemed to be a simple dilution effect. However, with gases such as sulfur dioxide and ammonia, reactions took place which led to precipitation.

The small cell with removable windows was used for these studies. The fluorescence window was aimed downward so that the precipitate would collect on it. Subsequent to precipitation, an infrared spectrum was run on the product. The spectrum for the sulfur dioxide product is shown in Figure 40.

It has been found[39] that sulfur dioxide and oxygen will form a polymer of the form



which is fairly stable. The sulfur dioxide and oxygen were passed through a discharge together. It is conceivable that since the sulfur dioxide was with the oxygen in the discharge apparatus, that ozone formed and immediately reacted with the

sulfur dioxide coating the walls of the apparatus. The fact that a precipitate was formed in this study seems to indicate that unexcited sulfur dioxide will react with ozone; i.e., the sulfur dioxide need not be passed through the "silent-discharge" apparatus to insure reaction.

The spectrum shown in Figure 40 was taken on the fluorescence window of the 44.5 centimeter cell after it was coated with the sulfur dioxide-ozone precipitate. It shows what seemed to be definite sulfate-type vibrations.

The ammonia gave a yellow-white solid which turned to a liquid when exposed to air. Consequently, no spectrum was run on this compound. Although these reactions were interesting, they did not really come within the scope of this endeavor. The precipitate might possibly be N_2O_5, formed by the following scheme:[40]

$$O_3 + NH_3 \rightarrow NO + H_2O$$

$$NO + O_3 \rightarrow NO_2$$

$$NO_2 \rightarrow N_2O_4$$

$$N_2O_4 + O_3 \rightarrow N_2O_5$$

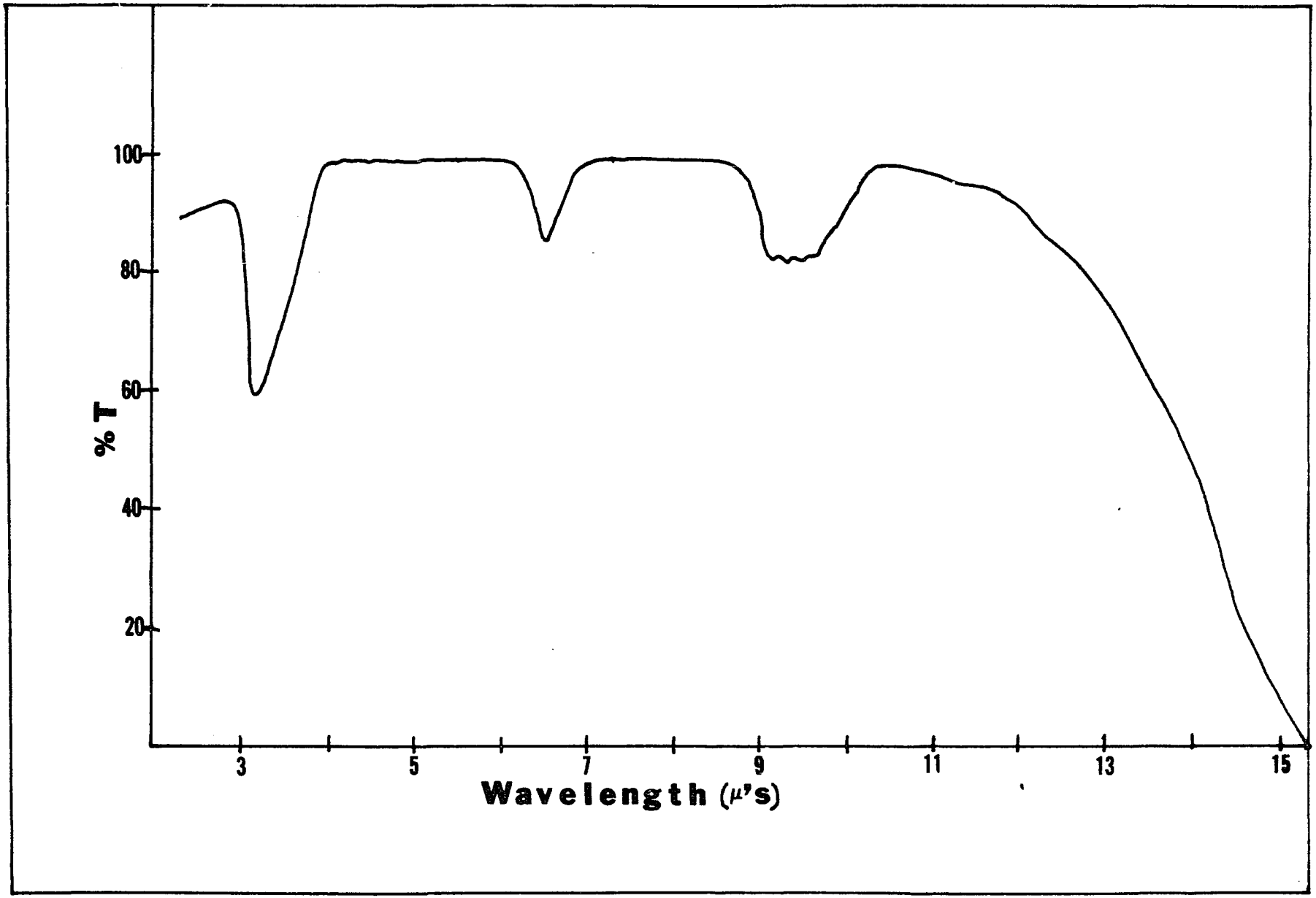
$$N_2O_5 + H_2O \rightarrow HNO_3$$

With the discovery of this type of phenomenon (i.e., extreme reactivity, it was decided that a good fluorescence collection system must be developed before any valuable information on interferents can be obtained.

Figure 40

INFRARED ABSORPTION SPECTRUM OF

SULFUR DIOXIDE-OZONE POLYMER


100
80
60
40
20
% T
3
5
7
9
11
13
15
Wavelength (μ's)

Two other pieces of information were obtained from these experiments. First, the reaction rate seemed to be increased by orders of magnitude, judging from the rate of precipitation, by passing the laser beam through the cell. In most cases, the products were observed to form immediately with the laser on, and very slowly (or never) with the laser off.

Second, the precipitates formed quickly on the inside surfaces of the cell until they were covered. The precipitation then seemed to stop.

These type of phenomena have been observed in this laboratory for other compounds.[41]

Part IV

REMOTE SENSING

INTRODUCTION

The next logical step in this study was to aim the laser out of the window and collect the fluorescence scattered back.

There were so many variables in this type of study that a large number of experiments had to be done to cover all the combinations of factors.

Both the tunable and the Perkin-Elmer lasers were tried and either the laser beam or the incoming radiation could be chopped. The experiment could be done with just the detector filter system, or with the monochromator.

The final set of variables were meterological. If the sun was shining, a higher background would be expected; if it were raining, increased scattering and interference would be expected from raindrops; and at the end of the day large fluxes in line current would be expected (when other workers were turning off their equipment) which would increase the instability of the detection system.

If the experiment had to be evaluated for all these conditions, some of which are undoubtedly interrelated, then analysis would be indeed complex.

Fortunately, this was not the case since most of the above either did not work, or made no difference.

DESCRIPTION OF EQUIPMENT

It was decided that the Cassegrainian collection system would be used to gather the scattered radiation from the atmosphere.

The laser then had to be aimed out the window and the collection system made coaxial with the laser beam. The laser beam would have to be made to fall on some object and the telescope system made to focus on that object. The object would then have to be removed.

The Chemistry Library is one and one-half stories higher than the laboratory, and due to the shape of the building it is visible from the laboratory window. If the laser beam was made to pass over the roof of the library, objects could be placed in and out of the beam easily. The edge of the roof is about fifty meters from the window.

The top of the laboratory table used is about ninety-four centimeters from the floor, and the bottom of the window is about sixty-five centimeters from the table top. The telescope system had to be aligned so that it cleared the window but passed less than two meters above the library roof or else it would not be possible to place objects in the path of the beam.

It was decided that if the Cassegrainian system parts were left attached to the large cell plates (Figure 7, Parts B and C) they could be clamped to a crude optical bench and brought to a height and angle to accomplish all alignment objectives.

Alignment

The object which was chosen to be placed in the beam to facilitate alignment was a retroreflector. This is a corner cube prism, purchased from Edmund Scientific, which reflects a beam of light back on itself no matter what angle the beam strikes it.

The helium-neon laser and a beam splitter were placed in the optical system in such a manner that the helium-neon laser beam hit the output mirror of the carbon dioxide laser and then went through the mirror system to the retroreflector back to the Cassegrainian system and was focused on the slits of the monochromator.

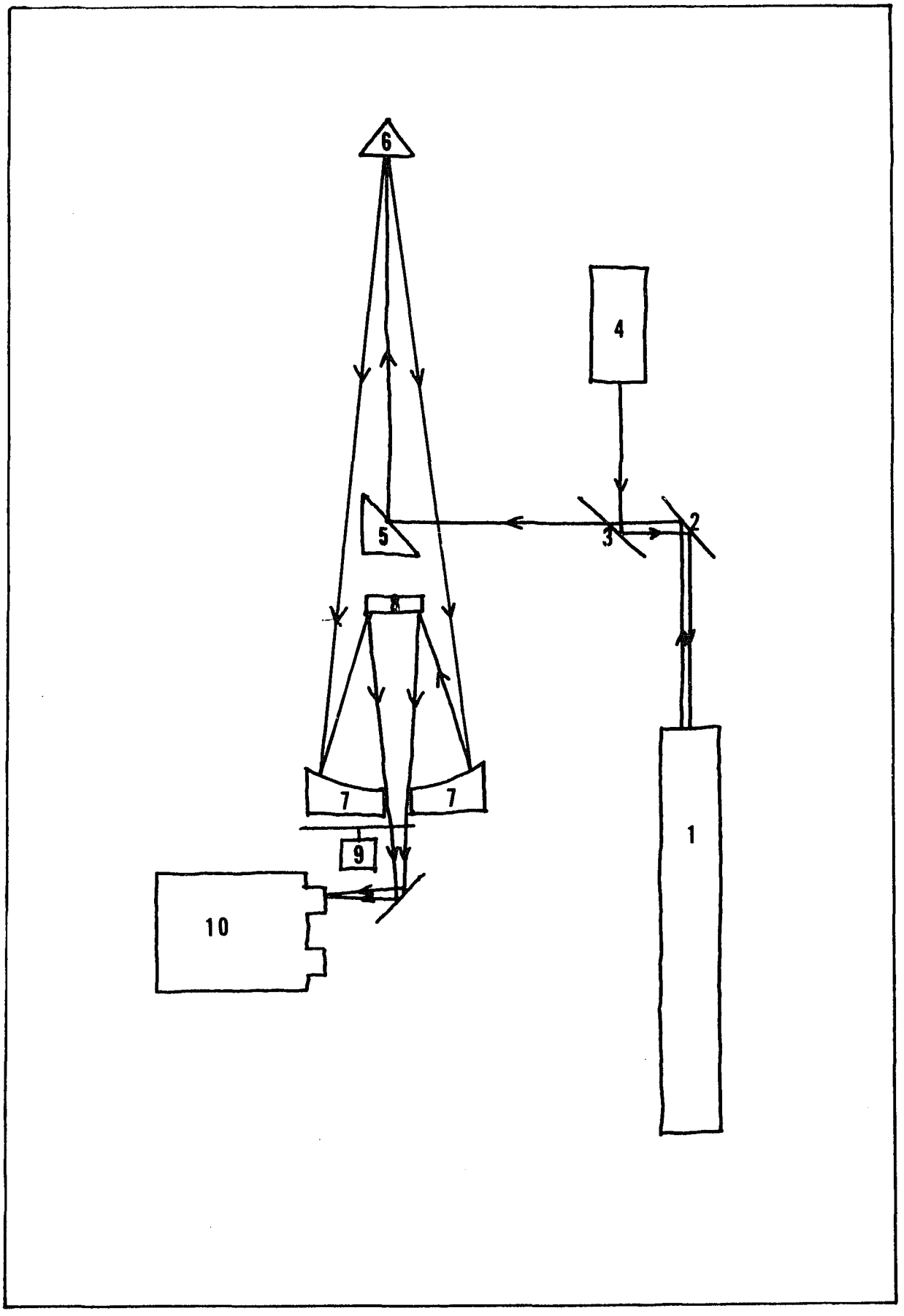
The remote sensing alignment layout is shown in Figure 41.

Mirror Two in Figure 41 is actually a composite of a number of mirrors, the exact number depending upon whether the tunable laser or the Perkin-Elmer laser was used. These extra mirrors were used to make the laser beam strike the final mirror at exactly the right angle.

Figure 41

LAYOUT OF REMOTE SENSING APPARATUS

1. Carbon Dioxide Laser
2. Mirror (actually a number of mirrors)
3. Beam Splitter (used only during alignment)
4. Helium-Neon Laser
5. Final Mirror
6. Retroreflector (used only during alignment)
7. Primary Mirror of Cassegrainian System
8. Secondary Mirror of Cassegrainian System
9. Chopper
10. Monochromator


6
4
5
3
2
7
7
1
9
10

The first step in the alignment procedure was to turn on the carbon dioxide laser and find the point where it passed over the edge of the roof. This was marked on a piece of cardboard attached to a stand. Then, the retroreflector, which was clamped to a ringstand, was placed in front of this spot. The helium-neon laser and beam splitter were then aligned so that the helium-neon laser beam hit the retroreflector. The reflected beam then was used to align the telescope system.

Divergence Measurements

The detector used to find the carbon dioxide laser beam was the human hand. It was observed at this time that the power of the laser at fifty meters was much less than that in front of the laser. It was further noted that the beam diameter of the carbon dioxide laser and the helium-neon laser seemed to be diverging much more than was expected. The helium-neon laser seemed to have increased in diameter by about a factor of eleven.

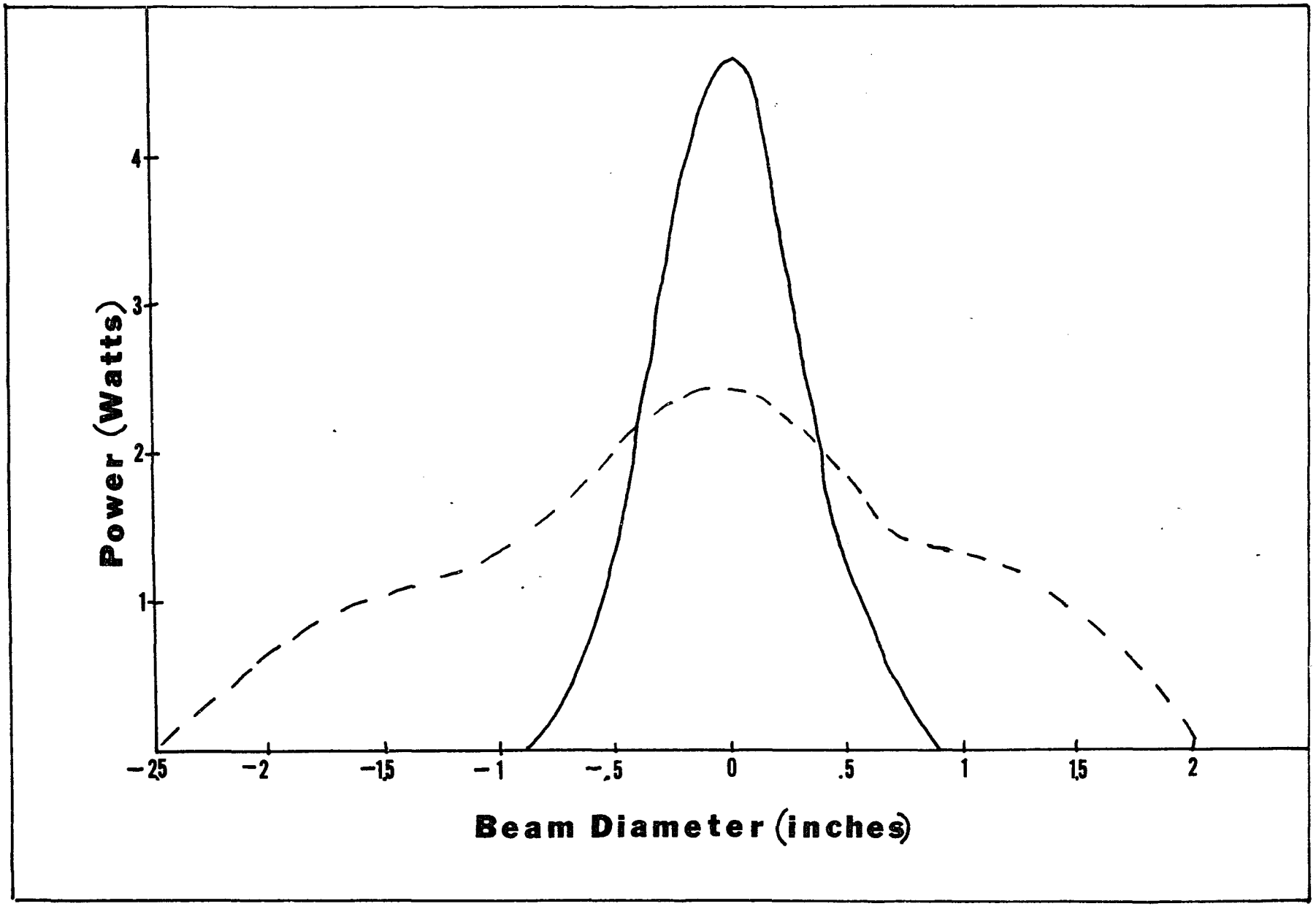
As a consequence of this, a crude apparatus was built to measure the beam diameter. The power meter head was placed on a stand with a ruler attached to it. The head was then moved across the beam and measurements of power versus ruler-readings were taken. The results of these measurements are shown in Figure 42.

At first, slits were placed in front of the power meter head, but they were abandoned because they decreased the

Figure 42

POWER VERSUS BEAM DIAMETER

Solid Line: At Window
Dashed Line: On Roof (Power x 10)


Power (Watts)
4
3
2
1
-2.5
-2
-1.5
-1
-.5
0
.5
1
1.5
2
Beam Diameter (inches)

sensitivity too much. The opening in the head is tapered to about one inch in diameter.

By integrating the power versus beam diameter measurements in Figure 42, it was seen that only about fifteen per cent of the power measured at the window was reaching the rooftop measuring point. This could have been due to either one or both of two effects--the radiation was absorbed or scattered away; or the beam was actually much larger but the power at the edges was too low to measure with the power meter.

The above measurements were done on the tunable laser, but the Perkin-Elmer laser seemed to diverge even more.

RESULTS AND DISCUSSION

The first thing which was done was to try the system with just the detector; i.e., with no monochromator. It was very difficult to shield the detector from stray laser radiation, especially when the beam was being chopped. With the incoming radiation being chopped, it was observed that there seemed to be an increase in signal when the laser was on. This was done using the 10.62 micron line of the tunable laser. The results were sporadic and did not seem to be affected by either time of day or meterological conditions.

This is contrary to what was expected, because rain drops should scatter better than dry air. Due to the fact that the beam was passing over a parking lot, it was hoped that in the afternoon when the automobiles were leaving, the resultant gaseous emissions would lead to an increase in signal.

Various lines of the tunable laser were tried and they all gave the same results. The scattered radiation was too weak to be detectable with the monochromator, so the technique was tried using the Perkin-Elmer laser.

At first it seemed that two strong signals were being observed; one at around seven microns, and another which consisted of the three lasing lines mentioned on page 42.

The three Perkin-Elmer lines were in the same power ratio as the unscattered lines and seemed to have just as narrow a bandwidth.

It was felt that since the lasers were diverging so much, that the observed signal might be coming from radiation scattered from Mirror Five (Figure 41). To correct this, two aluminum sheets with holes one inch in diameter were placed in the beam to columnate it further. One was placed between the laser and Mirror Two, and the other between Mirror Two and Mirror Five. The resonance scatter signal disappeared completely.

The laser power was measured in front of the laser and at the window of the laboratory, with and without the aluminum sheets. The output of the laser was twenty-nine watts at the time, but only sixteen watts were reaching the window of the laboratory. With these aluminum sheets, the power at the window dropped to eight watts.

As seen in Figure 26, seven microns is right where the grating efficiency curve for Filter Four is maximum. If the system was "seeing" background radiation, a rise in the signal would be expected at around seven microns. Therefore, although the seven-micron signal did not disappear when the aluminum sheets were inserted into the beam, it is suspect.

When an 800-900 degree Centigrade blackbody source (a Dutch Masters cigar) was placed on the roof in the field of

view of the detector system, no signal at 10.6 microns was detectable. This means that our sensitivity was very low indeed.

PARTICULATE AND OZONE ANALYSIS BY REMOTE SENSING

It was seen above that small changes in wavelength gave rise to large changes in the fluorescence intensity. This relationship would not be true for particulates; i.e., the scattering intensity should vary slowly with small changes in wavelength. This means that the laser could be tuned to a wavelength which generated fluorescence from ozone and one could look at the emission signal plus the scattering signal from the particulates.

It would then be possible to tune the laser to a wavelength which generated little or no ozone fluorescence and measure only the scatter from the particulates.

Based on the two signals obtained, it should be possible to calculate the ozone concentration and the particulate level. This technique should be particularly valuable at high altitudes where ozone concentration is high and particulate levels are low.

In any event, a correction should be made for ozone fluorescence where the wavelength coincides with a scatter peak used for particulate analysis.

Part V

CONCLUSIONS

CONCLUSIONS

It has been shown that a relatively small amount of ozone can give rise to a detectable signal, so that if a more efficient collection system were built, it would extend the detectivity range to a low value. Also, the fact that lasers are made quite a few orders of magnitude more powerful than either of ours, and that cryogenic detectors are available with at least two orders of magnitude more sensitivity than the detector used in this study, leads one to believe that the method can be used for remote sensing.

When a good collection method is devised, then the interferents of ozone can be studied. This part of the ozone problem will have to wait on that development.

Another encouraging fact was the high efficiency of the processes involved. If (as it seemed to be in the case of ozone) a large amount of the power absorbed was converted to emission, and not translational energy, this is another plus factor in the case for the remote method.

The fact that a small change in the wavelength of the laser can cause a large increase in the transmission and a large decrease in the emission leads one to think that one might be tuning between the pressure-broadened rotational lines in the absorption fundamental of ozone.

The technique should be capable of distinguishing between fluorescence and simple scattering. This mutual source of interference can be removed by using a tunable laser.

Part VI

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VITA

John Louis Guagliardo was born in New Orleans, Louisiana, on the fifth of October, 1945. He attended Holy Ghost Catholic School in Hammond, Louisiana from the first through the eighth grade. He received his secondary education at Hammond High School. He then attended Southeastern Louisiana University in Hammond and was awarded a Baccalaureate of Science in Chemistry on May 27, 1967; after which he entered Louisiana State University in Baton Rouge, Louisiana for graduate study.

The author is married to the former Elaine Allen, and they are the parents of one child, a daughter, Elizabeth Pierson.

EXAMINATION AND THESIS REPORT

Candidate: John Louis Guagliardo

Major Field: Chemistry

Title of Thesis: A Feasibility Study of Ozone Remote Sensing by Laser Induced Infrared Fluorescence

Approved:

J. W. Robinson
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

T. Shan

S P McGlynn

Eugene W. Berg

Nicholas Tisdale

Date of Examination: